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Volume XXIX April, 1930 Number 4

APR 14 1930

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PUBLISHED MONTHLY
THE WILLIAMS & WILKINS COMPANY
MT. ROYAL AND GUILFORD AVENUES
BALTIMORE, MARYLAND, U. S. A.

Made in United States of America

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REPLACEABLE BASES OF IRRIGATED SOIL[1]

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Received for publication September 12, 1929

The nature and amount of replaceable bases have been shown repeatedly to have a very important bearing upon the physical condition and the productiveness of soils. Moisture conditions, likewise, are known to have great influence upon physical properties and fertility. The effect of moisture conditions upon the replaceable bases, however, has not been extensively studied.

Rice soils exhibit very peculiar physical properties and offer unusual, and often difficult, fertility problems. Since rice is grown in soil submerged by water for about 75 days, it seemed desirable to determine the effect of excess water upon the replaceable bases. The results presented in the following pages were obtained for the purpose of contributing to the solution of this problem.

REVIEW OF LITERATURE

Conner (3) studied the effect of moisture content upon acidity as determined by three lime-requirement methods and the effect upon the amounts of various elements extractable with normal potassium nitrate. His results showed, in general, that the acidity of soils kept saturated with water for a period of time tended to decrease. The potassium nitrate extracts showed decided increases of iron in the case of soils kept saturated. Aluminum extracted by this means was increased in some cases but decreased in others, and manganese was decidedly increased in nearly every case. Calcium showed a tendency to decrease in the extracts from saturated soils, whereas magnesium tended to increase.

The effect of flooding a soil with sea water was studied by Page and Williams (11). They found that exchangeable calcium was decidedly decreased whereas exchangeable sodium, potassium, and magnesium showed increases. Sea water, however, has a much higher salt content, particularly sodium and magnesium chlorides, than has water that is used for irrigation purposes.

Gedroiz (4) found a very small increase in exchangeable calcium in soil submerged for 14 months in normal sodium chloride solution, the mixture being shaken for three minutes nearly every day.

[1] Contribution from the agronomy department, published with the approval of the director of the station. Research paper no. 153, Journal Series, University of Arkansas.

[2] Credit is due Mr. G. H. Banks, assistant director in charge of the Rice Branch experiment Station at Stuttgart, Ark., for taking most of the field samples and for furnishing the cropping history of the rice soil.

Martin and Christie (7) showed that the water-extractable calcium and magnesium of a sandy loam soil were decreased by waterlogging the soil for a period of several days.

Subrahmanyan (14) measured the hydrogen-ion concentration of soil submerged by water and found a progressive decrease over a considerable period of time. He also found an increase in free and saline ammonia. The writer working with Janssen (9) has shown a similar progressive decrease in hydrogen-ion concentration. This decrease largely disappeared when the soil was dried for a week before the determinations were made. This indicates that the decrease was due perhaps partly to ammonia and partly to reduction compounds resulting from the anaerobic conditions in the soil. The writer (8) has further shown that flooding a soil with distilled water for a period of 75 days caused a decrease in its exchangeable calcium and an increase in exchangeable magnesium. A small portion of the data from that work is repeated in this paper in order that it may be available for ready comparison with the other data reported here.

Schollenberger (13) puddled some Wooster silt loam, packed it in jars, and stored it for 3 weeks at 28°C. When the soil was removed from the jars, and exchangeable bases and reaction were determined it was found that the only significant changes had been a decrease in hydrogen-ion concentration and a decided increase in exchangeable manganese. He found no significant change in the ammonia content of the soil and concluded that the decrease of hydrogen-ion concentration was due to reduced forms of manganese.

MATERIALS AND METHODS

The soil used for the study of the effect of flooding with distilled water upon exchangeable bases was the surface soil of Clarksville silt loam. This is a residual soil derived from the weathering of a cherty, non-magnesian limestone of the Boone formation. It is a soil of medium fertility and has been cropped exclusively to non-irrigated crops. A quantity of this soil was finely pulverized and thoroughly mixed, and fifteen 200-gm. samples were weighed out and placed in wide-mouthed shaker bottles. Five of these were left air-dry, five flooded with distilled water until the water stood ½ inch above the surface of the soil, and the remaining five brought to 20 per cent moisture content, which is about optimum for the soil. They were then stored in a laboratory free from fumes and the moisture content was restored at frequent intervals. The samples were kept thus for 75 days, after which they were air-dried, then finely pulverized and subjected to analysis.

The rice soil studied is classified as Crowley silt loam and has been almost continuously cropped to rice for the past 18 years. Four horizons of the soil were studied. The boundaries of the horizons were established as accurately as possible but no attempt was made thereafter to make the samples, which were taken by means of borings, conform strictly to the horizon boundaries. The surface soil (horizon A) is a light gray silt loam, almost ashy when very dry,

with a rather high organic content and rather numerous, small iron concretions. Horizon A_1, extending from about 6 inches to about 14 inches below the surface, is rather compact, has a slightly bluish gray appearance, is not high in organic content, and has many iron concretions. Horizon B extends from approximately 14 inches below the surface to about 20 inches. It is lighter in color than the A horizons and has a low organic content and fairly numerous iron concretions. It is less compact than the A_1 horizon. Horizon B_1 extends from about 20 inches below the surface to a considerable depth. It is extremely tight and plastic, is bluish gray, and contains many very small iron concretions.

Similar samples were taken in an adjoining schoolyard from four horizons of soil of the same type but which has never been cropped to rice nor subjected to submergence. Replaceable bases were determined in these samples in order to furnish a basis for estimating the effect of annual applications of irrigation water upon the rice soil.

All soil samples were thoroughly air-dried and finely pulverized, and enough air-dry soil was weighed out to constitute 50 gm. of dry soil. This was then treated in an Erlenmeyer flask with 150 cc. of 0.04 *N* HCl. After standing for about 15 minutes, with frequent shaking, the soil suspension was thrown upon the filter and leached with successive portions of the acid solution until the leachings failed to respond to a qualitative test for calcium. Since 500 cc. always proved sufficient to remove all exchangeable calcium, all leachings were continued until that quantity was obtained.

Hydrochloric acid of 0.04 *N* strength was selected as the replacing agent because it was shown in the data presented by Kelley and Brown (6) that acid of that strength gave more nearly the same results as *N* NH_4Cl than did any other strength used. Preliminary results obtained by the author confirm these findings. Moreover, HCl was used in preference to a neutral salt because of the difficulty of removing the excess salt in a large number of determinations.

Calcium, potassium, iron, aluminum, and manganese were determined by standard methods. Sodium was determined by the method of Barber and Kolthoff, as adapted by Bray (2). Replaceable ammonia was determined by distilling the ammonia from the extract after it had been made alkaline, Nesslerizing the standard acid into which the ammonia was distilled, and determining colorimetrically. Magnesium was determined by the volumetric method proposed by Handy (5).

EFFECT OF SOIL MOISTURE CONTENT ON REPLACEABLE BASES

The results of this experiment with Clarksville silt loam are shown in table 1.

Calcium. These results were presented in a previous paper (8) and, as noted there, the only significant change was a depression of replaceable calcium due to flooding. This is in accord with the results of other investigators cited previously, though their results were obtained under somewhat different conditions.

TABLE 1

Effect of moisture content on replaceable bases of Clarksville silt loam

BASE STUDIED AND SAMPLE NUMBER		AIR-DRY		20 PER CENT MOISTURE		FLOODED	
		per cent	*M.E.**	*per cent*	*M.E.*	*per cent*	*M.E.*
Calcium	1	0.0924	4.62	0.0952	4.76	0.0832	4.16
	2	0.0912	4.56	0.0924	4.62	0.0808	4.04
	3	0.0900	4.50	0.0920	4.60	0.0808	4.04
	4	0.0916	4.58	0.0932	4.67	0.0824	4.12
	5	0.0912	4.56	0.0928	4.64	0.0804	4.02
	Average	0.0913	4.56	0.0931	4.65	0.0815	4.07
Potassium	1	0.0089	0.23	0.0097	0.25	0.0091	0.23
	2	0.0093	0.24	0.0103	0.26	0.0092	0.23
	3	0.0088	0.23	0.0094	0.24	0.0093	0.24
	4	0.0094	0.24	0.0102	0.26	0.0103	0.26
	5	0.0100	0.26	0.0091	0.23	0.0099	0.25
	Average	0.0093	0.24	0.0097	0.25	0.0096	0.24
Sodium	1	0.0032	0.14	0.0036	0.15	0.0033	0.14
	2	0.0034	0.15	0.0033	0.14	0.0037	0.16
	3	0.0030	0.13	0.0031	0.13	0.0032	0.14
	4	0.0034	0.14	0.0034	0.15	0.0038	0.17
	5	0.0036	0.15	0.0039	0.17	0.0037	0.16
	Average	0.0033	0.14	0.0035	0.15	0.0035	0.15
Magnesium	1	0.0086	0.71	0.0096	0.79	0.0201	1.65
	2	0.0091	0.74	0.0120	0.98	0.0206	1.69
	3	0.0086	0.71	0.0108	0.89	0.0201	1.65
	4	0.0096	0.79	0.0096	0.79	0.0158	1.30
	5	0.0086	0.71	0.0108	0.89	0.0192	1.57
	Average	0.0089	0.73	0.0106	0.87	0.0192	1.57
Aluminum	1	0.0111	1.23	0.0111	1.23	0.0212	2.35
	2	0.0103	1.14	0.0103	1.14	0.0254	2.82
	3	0.0114	1.26	0.0111	1.23	0.0209	2.32
	4	0.0096	1.06	0.0099	1.10	0.0247	2.74
	5	0.0135	1.50	0.0124	1.37	0.0263	2.92
	Average	0.0112	1.23	0.0110	1.22	0.0237	2.63
Iron	1	0.0195	1.04	0.0195	1.04	0.0418	2.25
	2	0.0223	1.18	0.0223	1.18	0.0376	2.02
	3	0.0209	1.12	0.0223	1.18	0.0446	2.36
	4	0.0223	1.18	0.0195	1.04	0.0349	1.87
	5	0.0195	1.04	0.0223	1.18	0.0418	2.25
	Average	0.0209	1.12	0.0212	1.13	0.0401	2.15

* M.E. = milligram equivalents per 100 gm. of dry soil

TABLE 1—*Concluded*

BASE STUDIED AND SAMPLE NUMBER		AIR-DRY		20 PER CENT MOISTURE		FLOODED	
		per cent	*M.E.**	*per cent*	*M.E.*	*per cent*	*M.E.*
Ammonia	1	0.0036	0.21	0.0029	0.17	0.0057	0.33
	2	0.0031	0.18	0.0030	0.18	0.0064	0.38
	3	0.0034	0.20	0.0027	0.16	0.0070	0.41
	4	0.0032	0.19	0.0032	0.19	0.0062	0.36
	5	0.0029	0.17	0.0033	0.19	0.0070	0.41
	Average	0.0032	0.19	0.0030	0.18	0.0065	0.38
Manganese	1	0.0316	1.15	0.0221	0.80	0.0448	1.63
	2	0.0320	1.16	0.0213	0.77	0.0430	1.56
	3	0.0318	1.15	0.0230	0.84	0.0426	1.55
	4	0.0290	1.05	0.0217	0.79	0.0419	1.52
	5	0.0345	1.25	0.0212	0.77	0.0408	1.48
	Average	0.0318	1.15	0.0219	0.80	0.0426	1.55

Potassium. No difference of any significance is revealed in the potassium data, differences in moisture content apparently having had no effect on replaceable potassium during the 75-day period.

Sodium. Differences in moisture content brought about no appreciable change in replaceable sodium content.

Magnesium. Keeping the soil at 20 per cent moisture content increased replaceable magnesium, but flooding brought about a decidedly greater increase. As with calcium, these results are taken from work reported in a previous paper.

Aluminum. Flooding the soil more than doubled the amount of aluminum extractable with .04 *N* HCl. No increase was shown in the case of the 20 per cent moisture treatment.

Iron. As in the case of aluminum, so with iron, flooding the soil decidedly increased the quantity removed by the acid. Again no significant increase was brought about by the 20 per cent moisture treatment. These results are in good agreement with those of Conner (3).

Ammonia. The quantity of replaceable ammonia was doubled by flooding the soil. Had the extracts been made from the soil before it was allowed to become air-dry, undoubtedly the amount of replaceable ammonia would have been considerably higher in the flooded soil and probably higher also in the soil with 20 per cent moisture treatment. Oxidation to the nitrate form very probably removed much of the ammonia during the drying process.

Manganese. Flooding produced a significant increase in replaceable manganese, while the 20 per cent moisture treatment produced a decided decrease. The increase in the flooded soil is in accord with the results obtained by Schollenberger (13), cited previously, though the difference is of lesser magnitude.

TABLE 2

Replaceable bases of four horizons of an old rice soil, Crowley silt loam

BASE STUDIED AND SAMPLE NUMBER		HORIZON A		HORIZON A_1		HORIZON B		HORIZON B_1	
		per cent	*M.E.*	*per cent*	*M.E.*	*per cent*	*M.E.*	*per cent*	*M.E.*
Calcium	15	0.1464	7.32	0.0700	3.50	0.0596	2.98	0.0900	4.50
	21	0.1328	6.64	0.1064	5.32	0.0700	3.50	0.1116	5.58
	101	0.0976	4.88	0.0808	4.04	0.0756	3.78	0.1272	6.36
	102	0.1116	5.58	0.0564	2.82	0.0700	3.50	0.1204	6.02
	106	0.1092	5.46	0.0716	3.58	0.0558	2.79	0.1504	7.52
Potassium	15	0.0052	0.13	0.0037	0.09	0.0125	0.32	0.0075	0.19
	21	0.0063	0.16	0.0052	0.13	0.0044	0.11	0.0062	0.16
	101	0.0059	0.15	0.0053	0.13	0.0063	0.16	0.0097	0.25
	102	0.0032	0.08	0.0028	0.07	0.0045	0.11	0.0073	0.18
	106	0.0035	0.09	0.0041	0.10	0.0057	0.15	0.0094	0.24
Sodium	15	0.0163	0.71	0.0146	0.63	0.0295	1.28	0.0386	1.68
	21	0.0133	0.58	0.0150	0.65	0.0191	0.83	0.0311	1.35
	101	0.0149	0.65	0.0181	0.79	0.0307	1.33	0.0366	1.60
	102	0.0167	0.73	0.0201	0.87	0.0286	1.24	0.0414	1.80
	106	0.0196	0.85	0.0230	1.00	0.0227	0.99	0.0472	2.05
Magnesium	15	0.0355	2.91	0.0192	1.57	0.0170	1.40	0.0278	2.28
	21	0.0321	2.64	0.0244	2.00	0.0191	1.57	0.0321	2.64
	101	0.0254	2.09	0.0182	1.50	0.0237	1.95	0.0422	3.47
	102	0.0259	2.13	0.0110	0.90	0.0233	1.91	0.0440	3.62
	106	0.0225	1.85	0.0206	1.69	0.0190	1.56	0.0552	4.54
Aluminum	15	0.0232	2.57	0.0390	4.33	0.0629	6.99	0.0605	6.72
	21	0.0151	1.67	0.0117	1.30	0.0163	1.81	0.0309	3.43
	101	0.0237	2.63	0.0249	2.76	0.0698	7.75	0.0289	3.21
	102	0.0228	2.53	0.0246	2.73	0.0532	5.91	0.0674	7.49
	106	0.0201	2.23	0.0235	2.61	0.0722	8.02	0.0713	7.92
Iron	15	0.0324	1.74	0.0648	3.48	0.0190	1.02	0.0201	1.08
	21	0.0313	1.68	0.0201	1.08	0.0223	1.20	0.0167	0.89
	101	0.0446	2.39	0.0302	1.61	0.0212	1.14	0.0156	0.84
	102	0.0391	2.10	0.0201	1.08	0.0201	1.08	0.0268	1.44
	106	0.0279	1.49	0.0201	1.08	0.0201	1.08	0.0145	0.79
Ammonia	15	0.0281	1.65	0.0279	1.64	0.0111	0.65	0.0092	0.54
	21	0.0276	1.62	0.0238	1.40	0.0053	0.31	0.0068	0.40
	101	0.0291	1.71	0.0291	1.71	0.0068	0.40	0.0107	0.63
	102	0.0320	1.88	0.0276	1.62	0.0082	0.48	0.0077	0.45
	106	0.0286	1.68	0.0267	1.57	0.0075	0.44	0.0077	0.45
Manganese	15	0.0364	1.32	0.0373	1.35	0.0263	0.95	0.0177	0.64
	21	0.0257	0.93	0.0323	1.17	0.0193	0.70	0.0226	0.82
	101	0.0369	1.34	0.0329	1.19	0.0294	1.07	0.0373	1.35
	102	0.0316	1.11	0.0292	1.06	0.0327	1.19	0.0373	1.35
	106	0.0351	1.27	0.0331	1.20	0.0289	1.05	0.0263	0.95

When the soil samples were leached with the acid it was observed that about one-third more time was required to leach those which had been flooded than the remaining samples. The increases in acid-extractable iron and aluminum suggest that this retarded rate of leaching may have been due to the presence of colloidal hydroxides of these elements.

The reaction of some of these samples was determined with the hydrogen electrode and it was found that there was only small variation within each group. The air-dry samples varied from pH 5.6 to 5.9; the 20 per cent moisture samples, from pH 5.4 to 5.6; and those which had been flooded, from 5.8 to 6.1. The reaction was determined after the samples had been air-dried.

The writer has noted repeatedly that a neutral salt used as a replacing agent removes far more iron from soil which has been flooded than from similar soil kept air-dry or at optimum moisture content.

EFFECT OF IRRIGATION OF RICE ON THE REPLACEABLE BASES OF FOUR HORIZONS OF CROWLEY SILT LOAM

The bases replaced from five samples of each of four horizons of Crowley silt loam cropped to rice for at least 15 of the past 18 years are shown in table 2.

The reactions of all the samples listed in table 2 were not determined, but the hydrogen-ion concentration of each of the four horizons of sample 102, which is fairly typical of the five samples studied, was determined with the hydrogen electrode. The results were as follows: horizon A, pH 7.3; horizon A_1, pH 7.0; horizon B, pH 5.2; and horizon B_1, pH 5.0.

The irrigation water obtained from several wells in soil similar to that from which these samples were taken and in the immediate vicinity has been partially analyzed by Bartholomew (1). His results show 9.3 p.p.m. of combined iron and aluminum and 67.2 p.p.m. of calcium. Other analyses furnished by A. H. Prince, former county agent of Arkansas County, show the average content of the water of several wells to be as follows: $CaCO_3$, 34 p.p.m.; $CaSO_4$, 11 p.p.m.; $MgCl_2$, 16 p.p.m.; NaCl and KCl, 27 p.p.m. Total mineral solids amounted to 96 p.p.m.

In order to compare the figures from this old rice soil with those from the same soil type in as near a virgin state as possible and never irrigated, samples were taken from four horizons of the soil in a school yard adjoining the 160-acre rice farm. This school yard was the only place available in the immediate vicinity where soil could be obtained that gave any promise of never having been cropped to rice or otherwise used in farming operations. This soil has not been cropped for at least 40 years, and perhaps never has been cultivated. Composite samples were made from borings taken in parts of the school yard that had been subject to very little tramping. The reaction of these samples as shown by the hydrogen electrode was as follows: horizon A, pH 4.6; horizon A_1, pH 4.0: horizon B, pH 4.6; and horizon B_1, pH 4.7. The reaction of each of the four horizons was decidedly more acid than was the case with the old rice soil.

The replaceable bases of these samples are listed in table 3.

Calcium. Replaceable calcium is decidedly more abundant in all four horizons of the old rice soil than in that never irrigated. There appear to be two zones of concentration; namely, horizon A, and horizon B_1. The higher content in the rice soil is probably due in part to the deposition of calcium salts by the irrigation water. Ogg and Dow (10) and others, however, have shown that the replaceable calcium of cultivated soil is more abundant, at least in many cases, than that of soil never cultivated.

Potassium. The lower horizons of the rice soil contain more replaceable potassium than the upper horizons. The reverse is true in the non-irrigated soil. This would suggest some leaching of potassium in the rice soil.

Sodium. Replaceable sodium is most abundant in the B_1 horizon of both soils. It is far more abundant, however, in the irrigated than the non-irrigated soil, in all four horizons. Perhaps the replaceable sodium in the B_1 horizon of

TABLE 3

Replaceable bases of four horizons of Crowley silt loam never irrigated

BASE STUDIED	HORIZON A		HORIZON A_1		HORIZON B		HORIZON B_1	
	per cent	*M.E.*	*per cent*	*M.E.*	*per cent*	*M.E.*	*per cent*	*M.E.*
Calcium	0.0792	3.96	0.0416	2.08	0.0368	1.84	0.0420	2.10
Potassium	0.0059	0.15	0.0032	0.08	0.0032	0.08	0.0035	0.09
Sodium	0.0093	0.40	0.0096	0.42	0.0116	0.50	0.0188	0.82
Magnesium	0.0271	2.23	0.0127	1.04	0.0086	0.71	0.0142	1.17
Aluminum	0.0750	8.33	0.0778	8.64	0.0769	8.54	0.0875	8.61
Iron	0.0178	0.95	0.0134	0.72	0.0123	0.66	0.0134	0.72
Ammonia	0.0017	0.10	0.0010	0.06	0.0011	0.06	0.0013	0.08
Manganese	0.0305	1.11	0.0173	0.63	0.0048	0.17	0.0026	0.09

the rice soil contributes to its impermeability. An impervious subsoil is a distinctly valuable feature of a good rice soil.

Magnesium. Magnesium has two rather distinct zones of concentration in the rice soil, the A horizon and the B_1 horizon. This is true also in the non-irrigated soil. The rice soil shows decidedly more magnesium in the B and B_1 horizons than the soil never cropped to rice.

Aluminum. In spite of the fact that the results obtained with the Clarksville silt loam showed that flooding increased acid-extractable aluminum, the soil never irrigated showed more aluminum in all horizons than did the rice soil. This may be because the hydrogen-ion concentration of the soil never irrigated was much greater than that of the rice soil. Aluminum was more abundant in the lower horizons of the rice soil than near the surface. It may contribute to impermeability in the subsoil.

Iron. As was the case with the Clarksville silt loam, flooding has increased the amount of acid-extractable iron in this soil, particularly in the A, A_1, and B horizons. Some of this iron may assume the form of colloidal hydroxide and increase impermeability.

Ammonia. It is rather to be expected that the anaerobic conditions existing in rice fields for a considerable period of time each year would bring about some accumulation of ammonia. The figures show this to be true in all four horizons, but particularly near the surface. The writer believes this ammonia is one of the factors responsible for the lesser hydrogen-ion concentration of the rice soil. Free ammonia is very probably partly responsible for the change of reaction toward alkalinity during submergence of soil with water, most of the change often disappearing when the soil is dried.

Manganese. Replaceable manganese in the three lower horizons appears to have been decidedly increased by flooding. If the acid extract had been obtained when the excess water had been reduced merely to the saturation point of the soil, much more manganese might have been obtained. Manganese also is very probably partly responsible for the reaction change during the existence of anaerobic conditions as proposed by Schollenberger (13). Robinson (12) also has found that manganese becomes very soluble in water-logged soil.

SUMMARY

The effect of moisture content upon the amount of calcium, potassium, sodium, magnesium, aluminum, iron, ammonia, and manganese extractable from Clarksville silt loam with .04 *N* HCl has been studied and the results are presented in the preceding pages. Soil was kept air-dry, at 20 per cent moisture content, and flooded for a period of 75 days.

Four horizons of an old rice soil also were studied, in comparison with four horizons of the same soil type (Crowley silt loam) never irrigated and in as near a virgin state as could be obtained.

The results for each of the various cations studied are discussed separately, following the presentation of the data.

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EFFECT OF LEAKING NATURAL GAS UPON THE SOIL

C. J. SCHOLLENBERGER

Ohio Agricultural Experiment Station

Received for publication September 19, 1929

Instances of damage to vegetation growing on soil beneath which leaks in pipes conducting natural gas are located, are of very common occurrence in regions where this fuel is utilized. In spite of the striking change in the appearance of the soil, however, no description of the chemical effects of exposure to the gas has been published, so far as the writer is aware. Such instances of gas injury as have been described have usually been studied by botanists, who have made very careful observations of the effects upon plants, but have said little or nothing about the effect upon the soil.

Sorauer (8) describes a case of gas injury to trees. He took samples of soil from about the gas pipe, noting that it was blue-black, and had an acrid odor resembling that of gas. He attributes both color and odor to the compact and unaerated nature of the soil (a filled-in swampy place), and reports that his chemist was unable to demonstrate acetylene or any other common constituent of the gas in the sample of soil. Apparently, the possibility that the abnormal properties of the soil may have resulted from previous exposure to gas was not considered. Harvey and Rose (4) studied the effect of gas upon root systems and performed much experimental work to determine which constituent of the gas is most injurious. They report that the odorous constituents of the gas which are absorbed and so persistently retained by the soil are relatively harmless to plants, but that the injurious effects of gas upon root systems can be duplicated by equivalent concentrations of ethylene in air. They think, therefore, that thorough aeration of the soil after leaks are stopped ought to enable newly planted trees to survive, although they quote Böhm (2) to the effect that long exposure to gas may make soil very toxic to seedlings.

All the references cited pertain to the effect of artificial gas, "illuminating gas," which varies widely in composition and is totally unlike natural gas, although this also is highly variable.[1] Nevertheless, the published descriptions

[1] Through the courtesy of Mr. Chas. F. Turner, chemist to The East Ohio Gas Co. of Cleveland, analyses of representative gas of the Wooster field were supplied.

	No. 1 per cent	*No. 2 per cent*
CO_2	0.1	0.1
"Illuminants"	1.8	0.6
O_2	1.8	2.2
CH_4	59.8	82.3
C_2H_6	30.1	9.0
N_2	6.4	5.8

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C_2H_6	30.1	9.0
N_2	6.4	5.8

of the effect of gas upon the soil would describe very accurately the effects of natural gas—killing of vegetation, blackening of soil, and a peculiar acrid odor suggesting gas.

A leak in pipes conducting natural gas from nearby wells to the station power house and crossing plot 30 on section C of the 5-year rotation fertility experiment afforded an opportunity for observance of the effects of the escaping gas upon both the soil and the crop planted on the plot. The pipes were laid during the fall of 1928 about 12 inches below the surface of the soil. Injury to oats was noted about two weeks after planting, and was evident in the yellow color of the seedlings. So far as is known, the germination of the grain was not affected, but the most badly injured oats soon ceased to grow, and died shortly afterward. Surrounding this 3- or 4-foot circle of plants entirely killed, was a zone of others greatly stunted, many reaching a height of only 4 or 5 inches with only one or two leaves and producing a single kernel at maturity. When pulled up, these badly stunted plants were found to have but a very small root system confined to the upper inch of the soil. As the distance from the leak increased, the plants appeared more nearly normal, until at 12 or 15 feet no injury was apparent. Borings in the soil most badly affected showed that the surface inch of the soil was somewhat darker than normal and the second inch considerably so, but the color was still predominantly brown. Below this, the color of the soil darkened rapidly, until at 6 inches it was blue-gray. At about 10 inches, the color began to lighten again and was nearly the normal yellow-brown at 12 or 14 inches. The odor of the blackened soil was suggestive of gas, but was more like that of stagnant mud from a pond bottom—the characteristic odor of soil long kept moist and warm under anaerobic conditions. At lower depths, the odor of the soil might be described as stagnant without much suggestion of gas. Besides differing from the normal soil in color and odor, the gassed soil appeared to differ somewhat in texture; the normal crumb structure of the soil was largely lost and the soil considerably puddled. It was also more moist at the time of sampling, but this was no doubt due to the more vigorous growth of the crop where not affected by gas.

On July 16, 1929, auger samples were taken from the plot to the depth of 6 2/3 inches, about a dozen borings being made in the spots worst affected and an equal number in parts of the plot where soil and crop were normal. The samples were passed through a 1/4-inch mesh screen to remove large stones and were mixed and examined at once, the results being calculated on the dry basis.

Moisture. The normal soil contained 12.45 per cent moisture, the gassed soil 19.28 per cent, when prepared for analysis as described.

Reaction was determined in 1:1 water suspensions by the quinhydrone

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Ethylene is absent and the so-called illuminants are saturated hydrocarbons, C_2H_8 and higher homologs. Hydrogen sulfide is absent, but a small amount of sulfur is present as CS_2 and organic polysulfides.

electrode method, the mixtures being mechanically stirred during measurement and the first reading taken as correct. The potential was found to be much less subject to drift in the suspension of the gassed soil than in that of the normal soil, which resembled in its behavior most samples of surface soil. As will appear later, this observation is significant in connection with McGeorge's (5) statement that the accuracy of the quinhydrone electrode is greatly affected by the presence of small amounts of manganese dioxide.

Ammonia. For determination of ammonia, 50-gm. samples of the moist soil were extracted by washing on a 10 cm. Buchner with 0.1 *N* HCl to a total volume of 1 liter, and aliquots of the extract were distilled with slight excess of sodium hydroxide into standard sulfuric acid.

Exchangeable bases. One hundred and twenty-five grams of the moist soil were packed in percolator tubes and leached with 750 cc. normal ammonium acetate at pH 7. This percolate was examined for exchangeable bases by methods described in other publications from this laboratory. Excess ammonium acetate was leached from the soil with neutral 80 per cent alcohol and the soil then distilled with sodium hydroxide, for determination of ammonium absorbed. At this point it may be well to note that the characteristic odor of the gassed soil was largely extracted from the soil and recovered unchanged in the distillate with the ammonia, indicating that it is due to a stable substance. Harvey and Rose (4) have made a similar observation with respect to the odorous principles absorbed from artificial gas by soil, and suggest that concentration of the odor by distillation may be useful in diagnosing gas injury.

Manganese in higher oxides. Attempts to use Brewer and Carr's (3) method for the determination of manganese dioxide in soil gave no useful results, as the same amounts were extracted from both samples—3.5 m.e. Mn per 100 gm. dry soil—whether or not ferrous sulfate was used with the sulfuric acid. Although Robinson (6) has reported that the reduction of manganese dioxide in soil by hydrogen peroxide is not quantitative, it was decided to try a method based upon this reaction. Fifty-gram samples of the moist soil were dispersed with 100 cc. water in a "drink mixer" for 20 minutes, then transferred to a liter Erlenmeyer with water to make nearly 500 cc. volume of liquid. After the addition of 3 cc. concentrated sulfuric acid to all, and 5 cc. 30 per cent hydrogen peroxide to one of each pair of duplicate samples, sufficient water was added to make the total weight that of 500 cc. liquid on the dry soil. The mixtures were shaken frequently for 30 minutes and then filtered, and manganese was determined in a 100-cc. aliquot of the filtrate by the bismuthate method, substantially as described by Blair (1). In the presence of peroxide, the total manganese extracted amounted to 3.6 m.e. per 100 gm. dry soil, the same amount as was obtained by the first method tried. Without peroxide, this method dissolved 0.5 m.e. Mn from the normal soil and 1.5 m.e. from the gassed soil. The difference between these figures, 1.0 m.e., should include exchangeable manganese, of which 1.6 m.e. had originally been found. For the 6 weeks that had elapsed since the determination of exchangeable manganese, the gran-

ular moist soil had been stored in a partly filled can that had been opened several times meanwhile. It was suspected that the discrepancy was due to a diminishing of exchangeable manganese during this storage period, therefore the determination was repeated. Exchangeable manganese found in the gassed sample after storage for 6 weeks under conditions probably favorable to oxidation amounted to only 0.004 m.e., a decrease of nearly 100 per cent. The exchangeable manganese had almost completely reverted to nonexchangeable forms, but nearly all of it remained more soluble in cold 1.1 per cent sulfuric acid than it had been in the normal soil. This experience indicates that the hot 1.1 per cent sulfuric acid used in Brewer and Carr's method will dissolve manganese dioxide in the absence of any added reducing agent, and that the same reagent, even when cold, is an active solvent for nonexchangeable manganese in soil. It seems that a more dilute or less active acid should be substituted for 1.1 per cent sulfuric acid. It is the opinion of the writer that 0.1 *N* nitric acid, or possibly acetic acid, would be a more satisfactory solvent; at any rate, hydrogen peroxide with dispersion is indicated to be as effective as ferrous sulfate with heat as a reducing agent for oxidized manganese in the soil, and in combination with an acid solution with minimum tendency to dissolve higher oxides of manganese should form the basis for a more satisfactory method of distinguishing the forms in which this element may occur in the soil.

RESULTS

The analytical data are presented in table 1. The samples differ in several important particulars, but the most striking difference between them is in the content of exchangeable manganese. The normal soil contains none, but manganese is very abundant in the salt extract of the gassed soil, amounting to 1.6 m.e. per 100 gm. dry soil, or 18 per cent of the total exchangeable bases. Although the determinations of manganese in higher oxides were unsatisfactory, both because the methods used were defective and because the soil's content of exchangeable manganese had changed before these methods were applied, the results obtained from one method indicate that the soil's original content of manganese in higher oxides was the source of the manganese which became exchangeable, and that under conditions favorable to oxidation the active manganese, in part at least, changed back to the oxidized form and became almost wholly inactive.

Exchangeable ammonium is notably higher in the gassed soil, no doubt as the result of biological action under the same abnormal and practically anaerobic conditions prevailing in the soil as appear to have resulted in the reduction of manganese dioxide (7). The origin of the ammonia can scarcely be considered as due to direct addition from the gas, as ammonia has never been reported as a constituent of natural gas, to the writer's knowledge.

The total absorptive capacity of the soil for bases is the same in both samples, but the degree of saturation by bases other than hydrogen is greater in the gassed

soil, so that its reaction is less acid. Exchangeable calcium and magnesium differ considerably in the two samples, and much more of both are present than would be expected considering that the plot has never been limed. A limestone macadamized road adjoins the plot, however, and much limestone dust has no doubt settled upon the plot; the topography is such that in times of exceptionally heavy rainfall some limestone might even be washed from the road onto the lower end of the plot, where no damage from gas was noted, and from which a part of the sample of normal soil was taken. For these reasons, no importance is attached to differences in contents of exchangeable calcium and magnesium. Potassium and sodium in exchangeable form are slightly higher in the gassed soil, which may be due to removal by the vigorously growing oats crop upon the normal soil. Iron in exchangeable form was absent from the ammonium acetate extracts of both samples, nor was any reaction for dilute acid-soluble sulfide obtained from the gassed soil, hence the blackening of the soil by gas was not due to formation of ferrous sulfide.

TABLE 1

Exchangeable bases in normal and gas-damaged soil

Expressed as milligram equivalents per 100 gm. dry soil

	EXCHANGEABLE BASES							MANGANESE SOLUBLE IN		REACTION pH
	Mn	Ca	Mg	K	Na	NH_4	NH_3 absorbed	Acid	Acid + H_2O_2	
	m.e.	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	
Normal soil	...	4.9	1.9	0.10	0.10	0.03	8.8	0.5	3.6	6.2
Gassed soil	1.6	5.2	0.8	0.14	0.14	0.08	8.8	1.5	3.7	7.1

AFTER EFFECTS OF GAS INJURY TO SOIL

It will be of interest to consider the available evidence as to the effect upon the future cropping capacity of the soil following repair of the leaking pipes. As has been stated, the sample of gassed soil had been kept moist in a partly filled and not strictly air-tight container, under conditions probably favorable to oxidation from the time of determining the exchangeable bases until the acid- and peroxide-soluble manganese was determined 6 weeks later. At this time a second leaching of gassed soil with neutral ammonium acetate for determination of exchangeable manganese only, was carried out. Exchangeable manganese found amounted to 0.004 m.e. per 100 gm. dry soil, a decrease of 99.75 per cent. The soil had lost most of its abnormal odor and the color was much lighter than it had been at first. A qualitative test for nitrate showed that an abundance was present. Small flower pots were filled with the two soils and seeded to wheat. This germinated and grew well, that in the pot of

gassed soil noticeably better. After the oats had been harvested and the plot plowed and fitted for wheat, it was noticed that volunteer oat plants were growing thriftily even where gas injury had been most severe, and this too where the leaks had not been repaired. Of course, these plants cannot be expected to survive after the soil has become compacted and the gas has again displaced the soil air. Robinson (6) cites a number of investigators who report that liming tends to cause the readily soluble manganese of the soil to change to insoluble forms, hence it may be predicted that in the case of a very acid soil damaged by gas, recovery would probably be hastened by an application of lime in addition to thorough aeration.

SUMMARY

The effect of leaking natural gas upon the soil is described. The soil is blackened and has a peculiar stagnant mud odor, as well as the acrid odor due to constituents absorbed from the gas. The most pronounced chemical effect upon the soil is shown by a great increase in exchangeable manganese content, and also by an appreciable increase in exchangeable ammonia. This increase in the active base content of the soil causes a lowering of the hydrogen-ion concentration. The source of the exchangeable manganese is in the higher oxides, which are abundant in many soils. The effects of the gas are thought to be due to displacement of air from the soil resulting in a biological reduction under anaerobic conditions so established, and are indicated to be quite transient. The exchangeable manganese quickly reverts to the non-exchangeable form under exposure to conditions favoring oxidation, and plants grow well in the soil. Recovery of very acid soils damaged by gas would no doubt be hastened by an application of lime in addition to thorough aeration.

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SOIL AND CROP STUDIES WITH AMMONIUM SULFATE[1]

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Received for publication September 25, 1929

The fertilizing value of ammonium compounds, especially ammonium sulfate, is already well known and much has been written on this subject. When acidity conditions in the soil are kept under control by the use of lime, ammonium sulfate ranks close to nitrate of soda as a fertilizer in producing good crop yields. It is also well known that chemical fertilizers when used continuously and in large amounts produce certain changes in the soil. These changes will vary according to the type and character of the soil.

In the present work an attempt has been made to study the effects of ammonium sulfate on different types of soil with special reference to the changes brought about in the soils when varying amounts were applied. The effects of this soil treatment on different crops were also studied and the nitrogen content of the plants determined. The experiments were carried on in pots during the late winter and spring months. The work was started in 1927 and continued in 1928 and 1929. The problem was attacked mainly from five points of view, namely:

1. To observe the effect of the fertilizer treatment on plant growth.
2. To observe the buffer effect of heavy and light soils in their ability to withstand large applications of ammonium sulfate.
3. To observe the changes in pH value under the different treatments.
4. To determine the "active" aluminum present in these soils.
5. To determine the nitrogen content of the crops.

The results of the experiments will be described under these headings.

One of the soils chosen for this work was a heavy silt loam having a pH value of about 6.7. The buffer effect of such a soil, on account of its high colloidal content, was thought to be ideal for a study of the effect of large applications of ammonium sulfate. Two-gallon pots each containing about 18 pounds of soil were used. Each pot received 4 gm. superphosphate, 2 gm. muriate of potash, and the nitrogen treatment was varied as follows:

Pot No.	*Treatment*
1	None
2	1.5 gm. Ammonium sulfate approximately equivalent to 367 pounds to the acre
3	3.0 gm. Ammonium sulfate approximately equivalent to 734 pounds to the acre
4	4.5 gm. Ammonium sulfate approximately equivalent to 1101 pounds to the acre
5	6.0 gm. Ammonium sulfate approximately equivalent to 1468 pounds to the acre
6	7.5 gm. Ammonium sulfate approximately equivalent to 1835 pounds to the acre

[1] Journal Series paper of the New Jersey Agricultural Experiment Station, department of soils, chemistry and bacteriology.

All treatments were run in duplicate. In one set of pots barley was grown and in another set rape. A duplicate experiment was set up using Sassafras sand. To insure a sufficient supply of iron and alumina, each pot received 0.25 gm. of ferric sulfate and 0.5 gm. of magnesium sulfate.

In 1928, the work was continued on the heavy soil, lettuce being used on the set of pots which previously had barley, and barley on the set which previously had rape. In 1929, barley and rape were grown in the same pots as in 1927. Each year the same application of fertilizer was made to each pot before planting as in 1927. Since it was learned in the first year's work that the Sassafras sand would stand only small applications of ammonium sulfate without causing severe injury, this experiment was not repeated the following year. Instead, a Sassafras sandy loam was used for a study of the effect of various applications of ammonium sulfate on a medium light soil. For this work 1-gallon pots containing 12 pounds of soil were used. The fertilizer application was cut down one-third in each case to correspond to the rate of application in the large pots. The crops grown in 1928 were lettuce and barley and in 1929 barley and rape. The results of the three years work in terms of crop yield, pH value of the soils, active aluminum content of the soils, and nitrogen content of the crops are given in tables 1 to 4.

DISCUSSION

Effect of fertilizer treatment on crop yield

An examination of the dry weights of the crops, as given in table 1, discloses some interesting facts. Where heavy silt loam was used there was no injurious effect on barley or rape by increasing the amounts of ammonium sulfate up to 1,800 pounds to the acre. Where lettuce was grown, however, the yield was cut down very markedly when more than 350 pounds of ammonium sulfate was used. No doubt lettuce is more sensitive to a high concentration of fertilizers and to acid conditions. With barley and rape, there was a gradual increase in the crop yield up to an 1,800-pound application, but in most cases the differences were not appreciable when more than 1,100 pounds of ammonium sulfate were applied to the acre. This would indicate that an application above that amount would not be practical even on a heavy silt loam. The conditions described are well illustrated in plate 1. Another fact that was clearly noticeable was that as the fertilizer application increased the plants became more succulent and had a tendency to droop unless supported. This, of course, was an indication that the plants were receiving more nitrogen than was needed. The plants receiving more than 350 pounds of ammonium sulfate an acre were a darker green than those not receiving so much nitrogen.

Where a Sassafras sand was employed there was a marked injurious effect on the crop yield when more than 350 pounds of ammonium sulfate was applied to the acre. When the application was over 1,100 pounds the crop was practically a failure. The growth of the plants and their dry weights are

exactly opposite to those grown on the silt loam. Plate 2 brings out these points very clearly.

A Sassafras sandy loam, having physical properties between those of the clay and sand, was also tried out. The crop yields with lettuce and carrots were similar to those on Sassafras sand. Even the 350-pound application of ammonium sulfate appeared to be too concentrated for these crops. Barley, however, was able to withstand the high applications of ammonium sulfate without any marked injury, although the maximum crop yields were obtained with the 700- to 1,100-pound application. Plate 3 brings out these facts more clearly.

TABLE 1

Dry weight of crops

(Average weight in grams of duplicate pots)

NITROGEN TREATMENT PER 18 POUNDS SOIL	POT NUMBER	SILT LOAM			POT NUMBER	SASSAFRAS SAND	POT NUMBER*	SASSAFRAS SANDY LOAM	
		1927 Barley	1928 Lettuce	1929 Barley		1927 Barley		1928 Lettuce	1929 Carrots
None	1	17.9	15.9	17.0	25	19.2	A	12.9	6.1
1.5 gm. $(NH_4)_2SO_4$	3	31.7	14.7	38.3	27	12.2	B	6.1	0.5
3.0 gm. $(NH_4)_2SO_4$	5	34.4	11.8	40.2	29	9.5	C	4.5	0.4
4.5 gm. $(NH_4)_2SO_4$	7	35.4	8.3	36.8	31	3.1	D	3.5	0.4
6.0 gm. $(NH_4)_2SO_4$	9	36.5	5.1	38.6	33	2.1	E	3.5	0.0
7.5 gm. $(NH_4)_2SO_4$	11	36.7	4.0	40.9	35	0.0	F	3.1	0.0
		Rape	Barley	Rape		Rape		Barley	Lettuce
None	13	11.0	27.4	15.5	49	35.8	G	29.0	11.3
1.5 gm. $(NN_4)_2SO_4$	15	30.1	36.1	31.2	51	34.5	H	32.3	4.9
3.0 gm. $(NH_4)_2SO_4$	17	37.9	39.3	42.2	53	15.2	I	35.1	2.2
4.5 gm. $(NH_4)_2SO_4$	19	43.9	37.0	43.0	55	13.1	J	36.5	0.9
6.0 gm. $(NH_4)_2SO_4$	21	39.1	38.8	52.9	57	2.4	K	31.7	0.8
7.5 gm. $(NH_4)_2SO_4$	23	42.0	39.5	49.8	59	0.0	L	30.6	0.6

* Pots A to L received only two-thirds of the nitrogen treatment as only 12 pounds of soil were used.

Buffer effect of heavy and light soils

From the data in table 1 on the crop yields and from the plates, it can be readily seen that the silt loam has a great capacity for absorbing large amounts of fertilizer and for protecting plant tissue from injury where the salt concentration is high. On the other hand, the Sassafras sand and even the sandy loam do not contain enough colloidal material to protect the plants against the concentration of fertilizer salts when used in more than moderate amounts. Of course it is realized that excessive amounts of ammonium sulfate have been applied in these experiments, but this only more strongly emphasizes the fact that caution must be observed when applying strong inorganic fertilizers to light soils.

pH values of the soils at different periods of time

In table 2 are given the pH values of the soils under different treatments and at various intervals of time. It may be borne in mind that preceding each crop there was a fresh application of fertilizer. Hence, the pH values of the silt loam as given in the column under the heading "after 2 years" represent soils that have had three applications of fertilizer during that period.

On the silt loam soil the pH values were considerably affected by the ammonium sulfate treatment even after one month. With no treatment the soil had a pH value of 6.6 and this was brought down to pH 6.0 in the course of one month by the application of 1,800 pounds ammonium sulfate to the acre.

TABLE 2

pH determinations of pot soils at different periods of time

NITROGEN TREATMENT TO 18 POUNDS SOIL	SILT LOAM SOIL					SASSAFRAS SAND		SASSAFRAS SANDY LOAM	
	POT NUMBER	pH after				POT NUMBER	pH after 10 months	POT NUMBER*	pH after	
		1 month	10 months	1 year	2 years				3 months	1 year
None	1	6.60	6.55	6.05	5.96	25	6.15	A	5.76	5.62
1.5 gm. $(NH_4)_2SO_4$	3	6.30	6.10	5.58	5.55	27	5.66	B	5.35	4.92
3.0 gm. $(NH_4)_2SO_4$	5	6.15	5.58	5.30	4.95	29	5.55	C	4.93	4.80
4.5 gm. $(NH_4)_2SO_4$	7	6.15	5.40	5.05	4.68	31	5.50	D	4.64	4.63
6.0 gm. $(NH_4)_2SO_4$	9	6.05	5.55	4.91	4.59	33	5.70	E	4.67	4.65
7.5 gm. $(NH_4)_2SO_4$	11	6.00	5.27	4.77	4.45	35	5.70	F	4.50	4.62
None	13	6.55	6.35	6.30	6.05	49	5.87	G	6.15	5.75
1.5 gm. $(NH_4)_2SO_4$	15	6.25	6.10	5.65	5.37	51	5.67	H	5.55	5.13
3.0 gm. $(NH_4)_2SO_4$	17	6.15	5.73	5.48	5.01	53	5.90	I	5.44	4.83
4.5 gm. $(NH_4)_2SO_4$	19	5.95	5.50	5.23	4.67	55	6.00	J	5.20	4.72
6.0 gm. $(NH_4)_2SO_4$	21	6.00	5.40	5.00	4.65	57	5.67	K	5.10	4.60
7.5 gm. $(NH_4)_2SO_4$	23	6.05	5.30	4.95	4.63	59	5.75	L	4.95	4.35

* Pots A to L received only two-thirds of the nitrogen treatment, as only 12 pounds of soil were used.

With 350 pounds it was brought down to 6.3. After 10 months, the pH had been lowered on the 1,800-pound application to 5.27 After the first and second year the pH values were brought down progressively lower with each application of ammonium sulfate and in proportion to the length of time. After the first year the pH range varied from 6.05 on the soils receiving no ammonium sulfate to 4.77 on the one receiving the highest amount. After the second year the variation in pH range was from 5.96 to 4.45. It will be noticed, however, that the crop yields of barley and rape on these soils did not fall off as the acidity increased. Apparently the strong buffer action of the silt loam prevented the increased acidity, due to free hydrogen ions, from hindering plant growth.

On the Sassafras sand the pH values were not changed so radically by the ammonium sulfate treatment. The pH was lowered 0.3 or 0.4 by the addition of 350 pounds of ammonium sulfate to the acre, but the acidity remained about the same with the higher applications. No doubt this is due to the fact that the base exchange capacity on the sandy soil is much less than the loam and thus fewer hydrogen ions would be set free. On the Sassafras sandy loam where the base exchange is greater again, the pH of the soils varied from 5.76 to 4.5 at the end of the 3-month period. However, after one year and a further application of fertilizer, these soils showed about the same pH as after three months with the exception of the soil that received 350 pounds ammonium sulfate. This soil decreased from pH 5.35 at the end of three months to 4.92 at the end of one year. According to these results it is evident that with an application of about 700 pounds ammonium sulfate to the acre the base

TABLE 3

"Active" aluminum found in pot soils under ammonium sulfate treatment

POT NUMBER	NITROGEN TREATMENT TO 18 POUNDS SOIL SILT LOAM	"ACTIVE" ALUMINUM 1927	pH 1927	"ACTIVE" ALUMINUM 1928	pH 1928
		p.p.m. Al_2O_3		*p.p.m.* Al_2O_3	
1	None	187	6.55	218	6.05
3	1.5 gm. $(NH_4)_2SO_4$			251	5.58
5	3.0 gm. $(NH_4)_2SO_4$			285	5.30
7	4.5 gm. $(NH_4)_2SO_4$	208	5.40	326	5.05
9	6.0 gm. $(NH_4)_2SO_4$			373	4.91
11	7.5 gm. $(NH_4)_2SO_4$	254	5.27	469	4.71
13	None	193	6.35	188	6.30
15	1.5 gm. $(NH_4)_2SO_4$			211	5.65
17	3.0 gm. $(NH_4)_2SO_4$			246	5.48
19	4.5 gm. $(NH_4)_2SO_4$	204	5.50	275	5.23
21	6.0 gm. $(NH_4)_2SO_4$			306	5.00
23	7.5 gm. $(NH_4)_2SO_4$	251	5.30	301	4.95

exchange capacity of the Sassafras sandy loam is slowed, at least as far as exchangeable hydrogen is concerned.

Presence of "active" aluminum in soils treated with ammonium sulfate

An attempt was made to determine whether there was any correlation between the amount of "active" aluminum present in a soil treated with varying amounts of ammonium sulfate and the pH value of such soils. "Active" aluminum (1) is that which is soluble in 0.5*N* acetic acid and is an arbitrary determination. However, since a weak acid is used, the amount of aluminum soluble in it gives a relative idea of the amount of easily exchangeable aluminum. It is also reasonable to suppose that by increasing the amount of ammonium sulfate in the soil more aluminum would be exchanged and brought into a more readily soluble condition. In a previous article (2) data were presented which indicated that sulfate of ammonia when used in large amounts or in

moderate amounts over a period of years tends to increase the amount of "active" aluminum in the soil. Also when used over a period of years without lime this salt materially increases the hydrogen-ion concentration. The data given in table 3 further substantiate this belief. After a period of one year the soil receiving no ammonium sulfate had 187 p.p.m. of "active" aluminum, that receiving 1,100 pounds ammonium sulfate an acre had 208 p.p.m., and the soil receiving 1,800 pounds ammonium sulfate had 254 p.p.m. The pH values were 6.55, 5.40, and 5.27 respectively. After the second year the same soils contained 218, 326, and 469 p.p.m. of "active" aluminum respectively and

TABLE 4

Total nitrogen content of crop samples (average percentage of nitrogen of duplicate pots)

NITROGEN TREATMENT TO 18 POUNDS SOIL	POT NUMBER	SILT LOAM			POT NUMBER	SASSAFRAS SAND	POT NUMBER*	SASSAFRAS SANDY LOAM
		Barley grain and straw 1927	Lettuce 1928	Barley grain and straw 1929		Barley grain and straw 1927		Lettuce 1928
None	1	1.005	1.268	1.032	25	2.502	A	1.831
1.5 gm. $(NH_4)_2SO_4$	3	1.390	2.615	1.400	27	3.234	B	2.860
3.0 gm. $(NH_4)_2SO_4$	5	1.852	2.494	2.194	29	3.209	C	3.543
4.5 gm. $(NH_4)_2SO_4$	7	2.460	4.147	3.095	31	4.158	D	3.739
6.0 gm. $(NH_4)_2SO_4$	9	2.601	4.389	3.403	33	4.291	E	3.475
7.5 gm. $(NH_4)_2SO_4$	11	2.922	4.424	3.443	35	No sample	F	3.713
		Rape	Barley grain and straw	Rape		Rape		Barley grain and straw
None	13	1.114	0.843	0.964	49	2.002	G	0.884
1.5 gm. $(NH_4)_2SO_4$	15	1.092	1.370	1.222	51	2.743	H	1.323
3.0 gm. $(NH_4)_2SO_4$	17	1.414	1.586	1.367	53	5.113	I	1.511
4.5 gm. $(NH_4)_2SO_4$	19	2.023	2.220	1.909	55	5.389	J	1.620
6.0 gm. $(NH_4)_2SO_4$	21	2.844	2.296	2.392	57	No sample	K	1.990
7.5 gm. $(NH_4)_2SO_4$	23	3.377	2.546	3.254	59	No sample	L	2.178

* Pots A to L received only two-thirds of the nitrogen treatment, as only 12 pounds of soil were used.

the pH values were 6.05, 5.05, and 4.71. On the soils receiving applications of ammonium sulfate in between the foregoing amounts the "active" aluminum was in proportion to the amount applied, and the pH values were lowered correspondingly. Hence, there appears to be a distinct correlation between the amount of "active" aluminum and the pH values. The formation of aluminum sulfate by base exchange reactions and the hydrolysis of this salt no doubt account for the increase in hydrogen-ion concentration.

Nitrogen content of the crop samples

The present work gave an excellent opportunity for determining the total nitrogen content of crops that had been grown under excessive nitrogen treat-

ment. The nitrogen was determined on the crops after they had been thoroughly dried and ground. In the case of the barley the heads were ground with the straw, therefore the analysis includes both grain and straw. Where no nitrogen was applied to the soil the barley ran about 1 per cent total nitrogen. The results are given in table 4.

As increasing amounts of ammonium sulfate were added to the silt loam soil the nitrogen content of the barley kept increasing, up to 2.922 per cent. When this same crop was repeated two years later, the nitrogen values on the dried samples were proportionately higher, the highest being 3.443 per cent with the 1,800-pound application of ammonium sulfate. It is interesting to note that with the Sassafras sand the percentage of nitrogen in the barley crop went up to 4.29, although the crop yield was very small.

Lettuce plants growing on the silt loam to which no nitrogen had been added contained 1.268 per cent nitrogen in the dry material. As ammonium sulfate was added to the soil in increasing amounts the total nitrogen content of the lettuce plants increased up to 4.42 per cent although the yield was proportionately cut down. Rape plants growing on the same soil increased in percentage of nitrogen from 1.114 to 3.377 and the crop yield also increased proportionately. On the Sassafras sand the percentage of nitrogen increased up to 5.385 but the crop yield decreased to a low point.

On the Sassafras sandy loam the percentage of nitrogen in the lettuce increased from 1.831 to 3.713 under the influence of the ammonium sulfate treatment, but again the yield was cut down very low. The barley crop increased from 0.884 per cent to 2.178 per cent nitrogen and the crop yield was not diminished except on the two highest treatments.

It is realized that very abnormal amounts of nitrogen have been found in these plants because of abnormal treatments. However, the significance of this nitrogen difference lies in the fact that the nitrogen content of the crops, and therefore the protein content, may be increased materially by having an ample supply of a nitrogen fertilizer in the soil. Just how much excess could economically be applied to increase the protein content of the crop and maintain a high yield is a question for each individual case and each particular type of soil.

SUMMARY

Pot experiments were conducted on three different types of soil using normal and excessive amounts of ammonium sulfate and growing various crops. The objects of the experiments were to study the changes brought about in the soils by such treatments and the effects produced on various crops. The problem was studied mostly from the point of view of crop yield, hydrogen-ion concentration of the soils, active aluminum content of the soils, and nitrogen content of crops. Some of the results may be briefly summarized as follows:

1. By increasing the amounts of ammonium sulfate up to 1,800 pounds an acre on a heavy silt loam there was no injurious effect on barley or rape but rather a gradual increase in the crop yield and in the percentage of nitrogen in the dry matter.

2. With barley, the nitrogen in the crop increased up to 3 per cent whereas with rape it increased to as high as 4 per cent.

3. On Sassafras sand, increasing amounts of ammonium sulfate beyond 350 pounds an acre showed marked crop injury. The injury was in proportion to the amount applied, as shown by the dry weights and by lack of germination. With the high fertilizer application, the nitrogen increased in the dry matter to over 4 per cent in the barley and to over 5 per cent with rape.

4. The protein content of the crops may be increased by an ample supply of nitrogenous fertilizer in the soil, but just how much excess can economically be applied to the soil is a question for each individual case and each particular type of soil.

5. After one month from the time the fertilizer was applied the pH had not changed more than 0.6 on the highest application of ammonium sulfate either on the loam or sand. After 10 months there was a difference of pH 1.3 on the highest application of ammonium sulfate on the loam soil. About the same conditions were brought about in the Sassafras sandy loam but the changes in pH were not so great on the sand. The base exchange capacity of these different types of soil no doubt influences the change in hydrogen ion concentration when different amounts of ammonium sulfate are applied. The strong buffer action of the loam soil prevents plant injury even though the hydrogen-ion concentration is increased.

6. There was found to be a distinct correlation between the amount of "active" aluminum found in the treated soils and their pH values. The formation of aluminum sulfate through base exchange reactions and the hydrolysis of this salt are thought to account for the increase in hydrogen-ion concentration of the soil.

REFERENCES

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PLATE 1

Effect on Plants of Different Amounts of Ammonium Sulfate on a Silt Loam Soil

All receive superphosphate and potash alike.

1. No nitrogen.
2. Ammonium sulfate equivalent to 367 pounds to the acre.
3. Ammonium sulfate equivalent to 734 pounds to the acre.
4. Ammonium sulfate equivalent to 1,101 pounds to the acre.
5. Ammonium sulfate equivalent to 1,468 pounds to the acre.
6. Ammonium sulfate equivalent to 1,835 pounds to the acre.

Fig. 1. Barley.

Fig. 2. Rape.

Fig. 3. Lettuce.

FIG. 1

FIG. 2

FIG. 3

PLATE 2

EFFECT ON PLANTS OF DIFFERENT AMOUNTS OF AMMONIUM SULFATE ON A SASSAFRAS SAND

All receive superphosphate and potash alike.

7. No nitrogen.
8. Ammonium sulfate equivalent to 367 pounds to the acre.
9. Ammonium sulfate equivalent to 734 pounds to the acre.
10. Ammonium sulfate equivalent to 1,101 pounds to the acre.
11. Ammonium sulfate equivalent to 1,468 pounds to the acre.
12. Ammonium sulfate equivalent to 1,835 pounds to the acre.

FIG. 1. Barley.

FIG. 2. Rape.

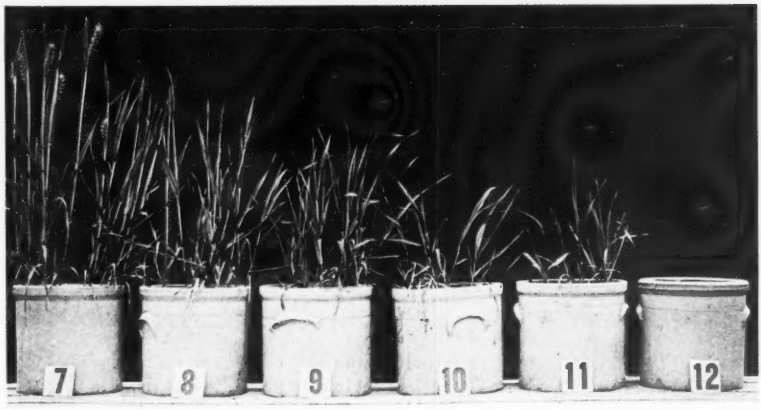

FIG. 1

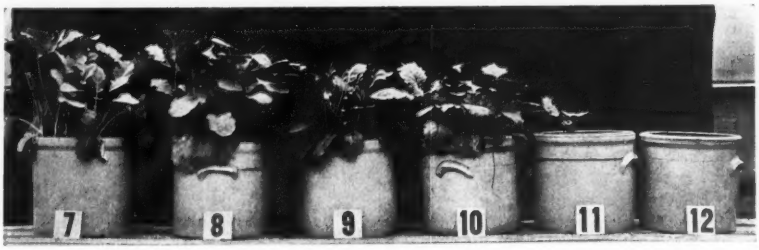

FIG. 2

PLATE 3

EFFECT ON PLANTS OF DIFFERENT AMOUNTS OF AMMONIUM SULFATE ON A SASSAFRAS SANDY LOAM

All receive superphosphate and potash alike.
19 and 13. No nitrogen.
20 and 14. Ammonium sulfate equivalent to 367 pounds to the acre.
21 and 15. Ammonium sulfate equivalent to 734 pounds to the acre.
22 and 16. Ammonium sulfate equivalent to 1,101 pounds to the acre.
23 and 17. Ammonium sulfate equivalent to 1,468 pounds to the acre.
24 and 18. Ammonium sulfate equivalent to 1,835 pounds to the acre.
FIG. 1. Barley.
FIG. 2. Lettuce.

FIG. 1

FIG. 2

EFFECT OF BURNING UPON THE ACCUMULATION OF ORGANIC MATTER IN FOREST SOILS

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Received for publication September 25, 1929

The utilization of the land resources of the United States is being placed on a more scientific and logical basis than ever before. This is not only a result of the economic conditions facing the country at present but is also due to a rapid and more extensive development of the investigation of those factors underlying the utilization of the land. The possible utilization of thousands of acres of the poorer sand lands in the southeastern coastal plains has focused attention on reforestation and the possible revenues to be obtained by following a system of logical and protected reforestation.

One of the greatest problems in the utilization of these poorer lands, however, has been the burning of forests and cut-over lands. The forestry service has been emphasizing for many years the injury to tree growth and to the possible future value of the timber, resulting from burning.

The protection of the forests and cut-over lands would allow organic residues to accumulate in the soil, and the subsequent effect of such an accumulation on the growth of the timber as well as on the possible future utilization of the land for cultivated crops has been suggested as very desirable. The organic matter problem is of great importance in the southeastern states where the temperature and rainfall, combined with the physical characteristics of the coastal plain soils, are favorable for an accelerated depletion of soil organic matter.

It is difficult to find a tract of land on the Florida peninsula which has not been burned over yearly for a number of years. The free range has led to a condition which predicates almost yearly burning of the cut-over lands in an effort to produce sufficient grass to maintain the range cattle. However, an island was located off Fernandina, Florida, on which the cut-over land and forest have not been burned for the past 42 years. The soil here is a Norfolk medium fine sand (deep phase).[2] For the purpose of comparing this soil with the soil of a burned area, a similar type of soil on the mainland near Gainesville, was sampled. This land has been burned over almost yearly for the past 42

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[2] Samples of soil were collected from the island through the courtesy of Mr. B. F. Williamson, president of the Florida Forestry Association.

years. The land on the island had a stand of virgin pine. The timber from the mainland soil had been removed within the past three years and the land left uncultivated. A fairly comparable soil condition in the two areas was prevalent during the 42 years, save for the burning factor.

Samples of soil were removed from both areas to a depth of 45 inches in the following layers: Leaf mold (present only on the island soil), 0-9 inches, 9–21 inches, 21–33 inches, 33–45 inches. A heavy leaf mold was present on the island soil but the mainland soil had only a growth of inferior range grasses.

TABLE 1

Analyses of forest soils from burned and unburned areas

Virgin Pine Forest—Norfolk Medium Fine Sand (deep phase)

DEPTH	MATERIAL*	ISLAND SOIL—UNBURNED AREA					MAINLAND SOIL—BURNED AREA				
		Organic matter	N	pH	Replaceable CaO	Hygroscopic H_2O	Organic matter	N	pH	Replaceable CaO	Hygroscopic H_2O
inches	*gm.*	*per cent*	*per cent*		*per cent*	*per cent*	*per cent*	*per cent*		*per cent*	*per cent*
Leaf Mold 4 in.	920 p. needle	96.20	0.600								
	415 intern.	93.33	0.700								
	2180 1 mold	58.87	0.715								
0– 9		2.542	0.042	5.10	0.0204	1.248	1.350	0.025	5.67	0.0300	0.553
9–21		1.336	0.021	5.50	0.0280	0.691	0.610	0.015	5.75	0.0215	0.418
21–33		0.967	0.014	5.84	0.0317	0.534	0.449	0.014	5.95	0.0181	0.233
33–45		0.607	0.015	6.10	0.0249	0.391	0.369	0.012	5.67	0.0190	0.179

Leaf mold and organic matter in leaf mold per square yard

	Leaf mold *pounds*	Organic matter *pounds*
Needles	2.03	1.95
Intermediate	0.92	0.85
True leaf mold	4.81	2.83

* Per square yard.

The soils were removed to the laboratory and carefully air-dried and mixed. The analyses included determinations of loss on ignition, total nitrogen, pH, exchangeable CaO, and hydroscopic moisture. The results of these determinations are given in table 1. Calculations of the organic matter and the nitrogen, in pounds to the acre, were made and are given graphically in figure 1.

From these analyses it appears that the protection of the forests on the island has lead to the conservation of the organic matter and nitrogen in this soil. A total loss of 121,289 pounds of organic matter to the acre by burning is shown. Calculated on the basis of 42 years that the island soils have been

protected, this amounts to an annual loss of 2,888 pounds an acre. A total loss of 1,126 pounds, or an annual loss of 27 pounds of nitrogen to the acre is indicated. It cannot be doubted that the burning depletes markedly not only

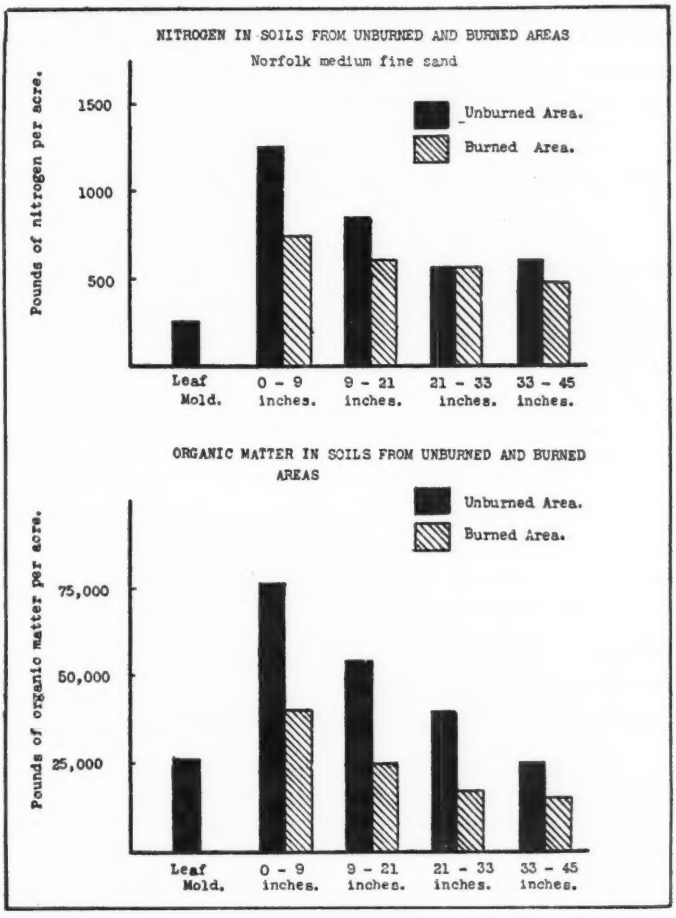

FIG. 1. NITROGEN AND ORGANIC MATTER FROM BURNED AND UNBURNED AREAS OF NORFOLK MEDIUM FINE LAND

the potential supply of the plant nutrients to the growing timber, but also that it destroys the potential organic matter supply of the soil.

There is a difference not only in the organic matter and nitrogen contents of these soils, but also in the exchangeable lime and in the hygroscopic moisture

content. These differences are no doubt associated with the differences in the organic matter content. Only in the 0–9 inch depth of soil did the replaceable lime content of the burned over land exceed that of the unburned land. This higher content of replaceable lime in the surface soil of the burned area is no doubt due to the accumulation of the ash constituents in the surface soil.

Table 2 gives the calculated percentages of nitrogen in the actual organic matter of the two soils. The percentage of nitrogen in the organic matter of the soil removed from the burned area is higher than that in the unburned

TABLE 2

Percentages of nitrogen in the organic matter of forest soils from unburned and burned areas

MATERIAL	NITROGEN IN ORGANIC MATTER	
	Unburned area	Burned area
	per cent	*per cent*
Pine needles	0.623	
Intermediate leaf mold	0.750	
Leaf mold	1.214	
0– 9 inch depth	1.652	1.852
9–21 inch depth	1.573	2.459
21–33 inch depth	1.447	3.118
33–45 inch depth	2.471	3.252

area. This indicates a more advanced stage of decomposition and failure to renew significantly the organic matter supply in the burned soils. The gradual increase in the percentage of nitrogen in the pine needles with their decomposition is correlated with the depth and evidently the age of the decomposing residues. The importance of the pine as a means of increasing the organic matter supply and the ultimate fertility of these deep phases of the Norfolk sands cannot be overemphasized, and the effects of burning over these lands distinctly interferes with the accumulation of organic matter in the soil.

METHOD FOR THE DETERMINATION OF INORGANIC NITROGEN IN DRIED PLANT TISSUE[1]

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Received for publication September 30, 1929

With the increasing use of nitrogenous fertilizers and the growing tendency toward the harvesting and grazing of young succulent plants, the inorganic nitrogen content of plants becomes an extremely important fraction. This fraction may represent as much as one-third of the total nitrogen of young well-nourished plants, or one and one-half to two per cent of their dry weight. Obviously, under such conditions the inorganic nitrogen fraction of plants demands recognition. Especially should this fraction be given careful consideration in the field of pasture management when studies are made relating to the influence of nitrogenous fertilizers upon the growth and protein content of young forage plants in relation to the proper time of harvesting and grazing. The cutting or grazing of plants at a time when a relatively high percentage of nitrogen is still in the inorganic or unsynthesized form results in a low yield of protein and lost efficiency of the nitrogen-bearing fertilizer used. Likewise, when the inorganic nitrogen supply is exhausted, protein synthesis ceases and, although the plant may continue to increase in weight, the additive materials are largely carbohydrate substances rather than of a proteinaceous character.

In a recent paper (2) a method was submitted by which the nitrogen as ammonia and the nitrate nitrogen of green plants can be determined with a high degree of accuracy. The method, however, necessitates the use of fresh green tissue and involves a thorough grinding and aqueous extraction of the tissue. This procedure is necessary when detailed analyses of the various nitrogen fractions are to be made and when it is desired to fractionate the inorganic nitrogen of the plant; but for many types of nitrogen investigations a knowledge of the inorganic, organic, and total nitrogen of the plant is sufficient. The total nitrogen can be determined accurately in dried plant tissue, even when the tissue is relatively high in inorganic nitrogen, provided the process is carried out in accordance with the precautions and directions given by Ranker (1).

The purpose of this paper is to present a method by which the total inorganic nitrogen of plant tissues can be determined quantitatively and with a high degree of accuracy on oven-dried material. The method is identical in every

[1] Journal Series paper of the New Jersey Agricultural Experiment Station, Department of Plant Physiology.

respect with the one previously submitted (2) except that in the present method no attempt is made to fractionate the inorganic nitrogen, and dried plant tissue is used, thus obviating the need of analyzing the plants immediately after harvesting. This method may prove highly useful in many types of plant investigations, since aliquot portions of the dried tissue can be taken, one used for total nitrogen determinations, the other for total inorganic nitrogen, the difference between the two representing the organic nitrogen of the plant. Thus the quantitative relationship between the synthesized and unsynthesized nitrogen fractions of the plants may be established.

APPARATUS AND METHOD

Immediately after the plant material is harvested, it is placed in an electric oven and dried at a temperature of 95° C. This dried tissue is then ground

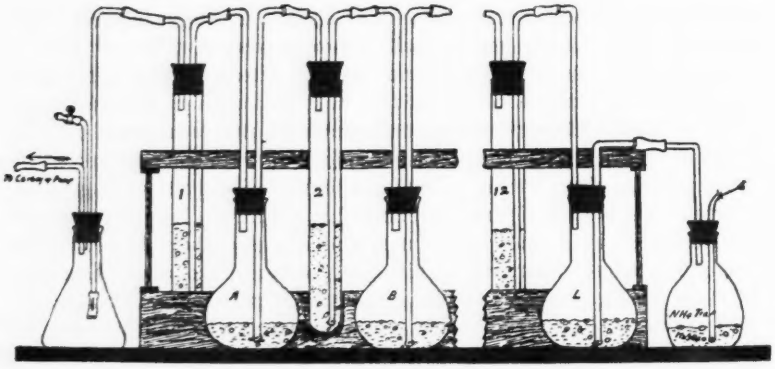

FIG. 1. THE ASPIRATION SYSTEM

sufficiently fine to pass a 30-mesh sieve. Two to five grams of the material, depending upon its inorganic nitrogen content, are accurately weighed and quantitatively transferred to a 300-cc. Florence aspirating flask. Then 70 cc. of water is added and the contents are allowed to stand for approximately one hour, being occasionally agitated by gentle revolution of the flask. After each agitation the plant material adhering to the sides of the flask is washed into the main body of the liquid, care being taken to use not more than 30 cc. of water in this process, since the flask should contain approximately 100 cc. of solution at the time of aspiration.

The aspirating system consists of large test tubes (2.5 x 25 cm.) used as absorption tubes and 300-cc. Florence flasks which contain the plant material. Twelve of each constitute a battery, and are so arranged that the same current of air is drawn through the entire system. Figure 1 shows the essential features of the apparatus and its arrangement. Beginning with flask *A*, which con-

tains the solution, 15 gm. of sodium chloride and 3 to 4 gm. of Devarda's alloy which has previously been ground fine enough to pass a 100-mesh sieve, are added. Sufficient sodium hydroxide is now introduced to make the contents of the flask approximately one-seventh normal, the stopper of the flask is immediately inserted, and connection is made by means of a short piece of rubber tubing between the outlet tube of the flask and the inlet of the absorption tube 1, which contains the standard acid. A slow current of air is now started through the solution of the first unit of the system, comprising flask *A* of the diagram and its corresponding absorption tube 1. In a similar manner the second unit of the system is prepared and joined to the first by means of a short rubber tube connection, as indicated in the diagram. Each unit is thus prepared and joined in the series in regular order until the battery is completed. Aspiration is allowed to proceed slowly at first, then rather vigorously for approximately 12 hours. Excess frothing may be prevented by the addition of 1 to 2 cc. of light paraffine oil and 2 or 3 drops of capryl alcohol.

Aspiration is accomplished by the use of an ordinary filter pump attached to a water faucet. With average water pressure, four batteries consisting of 12 units each can be aspirated from one pump by interposing a large carboy between the apparatus and the pump and attaching the several batteries to the aspiration pump through the carboy.

After aspiration has continued during the required period of time, the system is disconnected, starting with the flask and tube farthest removed from the suction pump and working forward. It is best to have a small current of air passing through the system while this is being done. The standard acid is now titrated and calculations made for the inorganic nitrogen found in the tissue.

EXPERIMENTAL

In testing the method here described the total inorganic nitrogen fraction was determined on the *dried* portions of the same plant tissues used in the previously published method (2) and the results of the two methods were compared.

Merck's analytical reagents were used throughout. The standard solutions used were standardized against benzoic acid obtained from the United States Bureau of Standards (sample 39 C). Methyl red was used as an indicator, and all titrations were carried to the complete disappearance of any red tinge.

After the plants were harvested, they were cut into ½-cm. pieces and thoroughly mixed. This minced tissue was halved. Inorganic nitrogen was determined on the green portion; and the other portion was dried, weighed, and transferred to the aspiration flasks, and inorganic nitrogen determinations were made as described in the foregoing. The results of these analyses, together with a brief description of the plants used, are given in table 1. The results are reported as the percentage of nitrogen present in the plants in the inorganic form as calculated on the dry weight basis.

Samples 1 to 12, which include the oat plants grown in the soil and the two groups of tomato plants grown in culture solutions, were analyzed by both methods immediately after harvesting. Four analyses were run upon aliquot samples of these three groups of plants and the data from these quadruple determinations, as well as their averages, are presented. The analyses of the

TABLE 1

Data showing accuracy of method in determining the inorganic nitrogen content of dried plant tissue

PLANTS USED*	SAMPLE NUMBER	TOTAL INORGANIC NITROGEN		
		By method of extracting green tissue	By analysis of dried tissue	Difference
		per cent	*per cent*	*per cent*
Oats from soils	1	1.227	1.262	0.035
	2	1.225	1.260	0.035
	3	1.225	1.248	0.023
	4	1.226	1.262	0.036
	Average	1.226	1.258	0.032
Tomatoes from culture solutions	5	0.365	0.363	0.002
	6	0.365	0.363	0.002
	7	0.362	0.363	0.001
	8	0.361	0.354	0.007
	Average	0.363	0.361	0.002
Tomatoes from culture solutions	9	0.331	0.329	0.002
	10	0.325	0.320	0.005
	11	0.331	0.320	0.011
	12	0.325	0.320	0.005
	Average	0.328	0.322	0.006
Oat plants grown in culture solutions having different salt proportions	13	0.900	0.898	0.002
	14	2.375	2.320	0.054
	15	1.800	1.824	0.024
	16	2.171	2.179	0.008
	17	1.931	1.889	0.042
	18	1.512	1.495	0.017
	19	1.978	1.950	0.028
	20	2.169	2.162	0.007
	21	1.263	1.227	0.036
	22	1.269	1.225	0.044

* All these plants were in the late vegetative phase of development when tests were made.

dried tissue of samples 13 to 22 were not made until 10 months after the green plant portions had been analyzed. In every instance, the data obtained by the two methods show very good agreement. In only one instance did the inorganic nitrogen of the plants as obtained by the two methods differ by as much as 0.05 per cent. In the majority of cases, the analytical data obtained by the two methods differed by less than 0.01 per cent.

From a consideration of the data here presented and of those obtained from many other tests of the method here described but not included in this report, it is quite evident that the inorganic nitrogen content of plants can be determined on their dried tissues with a relatively high degree of accuracy. The present method, however, has not been presented with the intent that it should replace the former one, which involves the use of the fresh green tissue, since in the fractionation of both the organic and inorganic nitrogen of the plant tissues, analysis of the fresh green tissue appears to be essential; and the former extraction method has been found to be quite accurate and highly useful in making quantitative studies of the inorganic nitrogen of plant tissue. In many types of investigation, however, the present method will prove to be highly useful, since the tissue can be prepared and treated in the same manner as is done in normal Kjeldahlization, and aliquots of this dried tissue can be used for total inorganic nitrogen determinations.

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RELATION OF THE AMOUNT AND NATURE OF EXCHANGEABLE CATIONS TO THE STRUCTURE OF A COLLOIDAL CLAY[1]

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Received for publication October 2, 1929

The effect of exchangeable cations upon the structure of soils has been distinctly evident from the wide differences in the properties of a soil saturated with the Na ion and one saturated with the Ca ion. The former is highly dispersed, viscous, and sticky when wet. Calcium saturated soils possess a more porous structure. Hissink (23), de Sigmond (13), Kelley and Brown (25), Gedroiz (21), and others have shown that the colloidality of a soil and its physical properties and structure depend on the state of saturation of the soil and the nature of the exchangeable bases. Gedroiz (20) considers the soil exchange complex in a state of unsaturation with bases as representing gels of hydrophilic colloids. These colloidal substances, unsaturated or saturated with monovalent bases, are supposedly in a semi-reversible condition (19). They pass into an irreversible state when saturated with the divalent ions. He observed that the dispersion of his soils followed the series: Na > NH_4 > K > Mg > H > Ca > Ba.

De Sigmond (14) found that soils saturated with Na ions were similar in their properties to Na-saturated, artificial zeolites. They possessed a puddled structure. A granular structure was produced by replacing Na with the Ca ion. Best results were obtained when as many millimols of $CaSO_4$ were used as there were millimols of exchangeable Na_2O and K_2O in the zeolite. Gallay (18) states that Ca must be added in excess of the total absorptive capacity in order to benefit the structure of a soil. Hissink (23) reports that the Ca ion produces flocculation when the soil is 95 per cent saturated with this cation. These differences are perhaps due to the method used for determining the absorptive capacity and to variations in the nature of the colloidal material.

Sokolovski and Lukaschewitsch (36) found that the resistance and plasticity of a soil were increased by replacing Ca with Na and NH_4 ions. Ca- and Mg-saturated soils were loose and crumbled very easily. The pressure resistance of soils saturated with various cations followed the series: Na > NH_4 >

[1] A part of a thesis submitted for the degree of doctor of philosophy. Published with the approval of the director of the Missouri Agricultural Experiment Station, Columbia, Mo.

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Mg > Ca > H. Mattson (31) observed that an electrodialyzed soil was more highly dispersed than the Ca-soil. Swelling of the colloidal material extracted from Sharkey clay was greatest according to the ionic order of Na > Ca > H. Charge followed the progression: Na > H > Ca. Anderson (1) reports that the heat of wetting and adsorption of water by colloids saturated with various cations followed the order: Ca > Mg > Na > H > K. A different progression was observed for the effect of cations on swelling, moisture equivalent, migration velocity, and pH; namely, Na > K > Ca > Mg > H. Anderson concludes that the influence of substituted cations on the properties of clay is usually directly proportional to the extent of their substitution. Mattson's results, however, do not support this conclusion.

Thomas (39, 40, 41) reports that the dispersion of soils, the percentage of water in soils at different vapor pressures, and soil structure are influenced materially by the nature of the exchangeable cation. Parker and Pate (33) have shown that the saturation of soils with monovalent bases causes a considerable reduction in the heat of wetting but that water absorption is practically unaffected.

Similar results were obtained by the author (2) in comparing the effect of different cations on the physical properties of soils. The Na- and K-saturated soils were found to have the lowest heat of wetting and moisture absorption, the K ion having the larger diminishing influence. These same soils were the most highly dispersed. The Na ion greatly increased the moisture equivalent values. The Na and K ions caused a lowering of the plasticity limits. The plasticity number of the Na-saturated soils increased; that of the K-saturated soils decreased. Ca-saturated soils containing a large percentage of clay were distinctly flocculated.

It is the purpose of this paper to present a study of the relation of various cations to the structure of colloidal clay. This investigation includes the following measurements: (*a*) reaction and conductivity changes; (*b*) flocculation values; (*c*) cataphoretic velocities; (*d*) particle sizes; and (*e*) viscosity changes. A detailed description of the experimental procedure is given in another publication (3).

EXPERIMENTAL

Electrodialyzed clay from the heavy layer of the Putnam silt loam was saturated to different degrees with Li, Na, K, Mg, and Ca ions by titrating the acid clay, prepared by electrodialysis, with the respective hydroxides. This procedure produces a clay containing the cation of the base on the exchange complex without the introduction of an anion except the OH ion, which forms water with the H ions replaced from the clay. The reaction involved is expressed by the equation:

$$\text{H}-\text{clay} + \text{NaOH} \rightleftharpoons \text{Na}-\text{clay} + \text{HOH}$$

This method provides a means of preparing different clay systems with a high degree of purity with respect to the added cations (8). Leaching with neutral

salts has been the most widely used method for saturating clays with various cations. This method, however, has two major disadvantages: (*a*) the addition of an anion which cannot be removed from the system, and (*b*) the inability to control rather definitely the quantity of cations in the colloid. The anion effect in the behavior of colloidal systems has often been overlooked in the interpretation of results.

The saturation capacity of the clay for bases was determined according to the conductometric and potentiometric methods suggested by Bradfield (7). This value was 57 milliequivalents to 100 gm. of clay, confirming all previous results obtained with this particular clay.

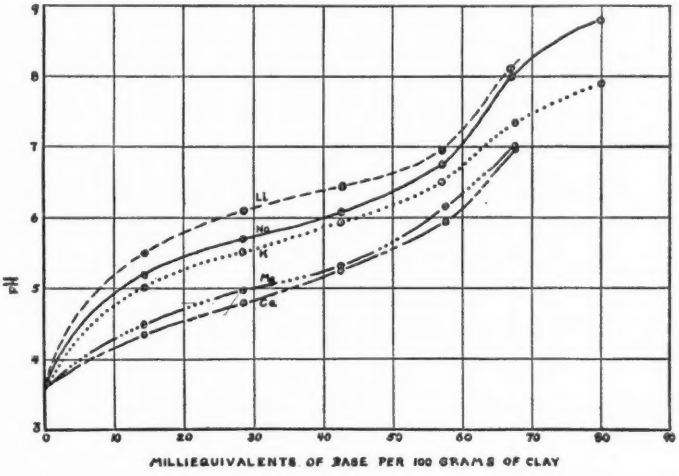

FIG. 1. CHANGE IN REACTION OF CLAYS CONTAINING VARIOUS AMOUNTS OF DIFFERENT CATIONS

REACTION AND SPECIFIC CONDUCTIVITY STUDIES

The change in reaction of these clays as a function of the amount and nature of the exchangeable bases on the absorbing complex was measured by means of the quinhydrone and hydrogen electrodes. The pH values of these sols are given in table 1. Titration curves are shown in figure 1. The results confirm the acid nature of this clay as reported by Bradfield (5). The clay is strongly buffered throughout most of the pH range. The lyotropic effect of the added cations is very evident from these curves. The Li ion, with its high hydration, is loosely bound to the particle, thereby undergoing a surface dissociation greater than any of the other less hydrated ions and causing a larger increase in the pH values. This dissociation tendency increases with hydration according to the series: Li > Na > K > Mg > Ca. Anderson (1) reports a similar

series for the pH values of clay saturated with different ions, except that the Ca-clay had a slightly higher pH than that of the Mg-clay. His clays, however, were saturated by leaching the soils with the chlorides of neutral salts, and the inability to remove all of the chlorides may account for this difference.

TABLE 1

The effect of the amount and nature of exchangeable cations upon the reaction, specific conductivity, viscosity and migration velocity of colloidal clay

ION	MILLIEQUIVALENTS PER 100 GRAMS CLAY	pH	SPECIFIC CONDUCTIVITY. MHOS × 10^5	VISCOSITY TIME IN SECONDS	MIGRATION VOLOCITY μ PER SECOND 1 VOLT PER CM.
H	57.00	3.61	5.00	64.7	2.70
Li	14.25	5.52	4.70	62.2	2.86
	28.50	6.10	6.96	67.2	3.04
	42.75	6.45	9.12	68.4	3.25
	57.00	6.95	14.66	63.5	3.53
	67.00	8.12	21.90	61.0	2.96
	218.00	>10.00	477.00	81.4	3.00
	536.00	>10.00	1,342.00	280.0	....
Na	14.25	5.26	5.58	61.4	2.73
	28.50	5.71	8.26	65.0	2.97
	42.75	6.07	10.71	67.2	3.19
	57.00	6.75	18.23	63.2	3.57
	67.00	7.99	25.51	60.6	2.86
	80.00	8.80	45.58	58.0	2.80
	218.00	>10.00	563.60	58.2	2.88
	536.00	>10.00	1,581.00	230.0	....
K	14.25	5.03	4.54	57.8	2.68
	28.50	5.52	6.32	60.2	2.88
	42.75	5.96	7.60	64.2	3.21
	57.00	6.50	15.34	64.2	3.47
	67.00	7.34	20.40	62.2	2.70
	80.00	7.90	39.50	59.0	2.67
	108.87	>10.00	100.02	57.9	....
	217.75	>10.00	469.30	190.0	....
Ca	14.25	4.36	4.40	61.0	2.39
	28.50	4.79	3.70	57.4	2.32
	42.75	5.28	3.80	56.4	2.19
	57.00	5.95	6.90	56.6	2.11
	67.00	6.95	13.90	61.0	2.08
Mg	14.25	4.50	3.71	57.1	2.50
	28.50	4.97	3.58	56.4	2.45
	42.75	5.31	3.87	56.4	....
	57.00	6.19	8.37	56.4	2.32
	67.00	6.98	16.53	60.0	2.31

The specific conductivity of these clay suspensions is shown in table 1 and figure 2. These data are characterized by a break at about 59 milliequivalents,

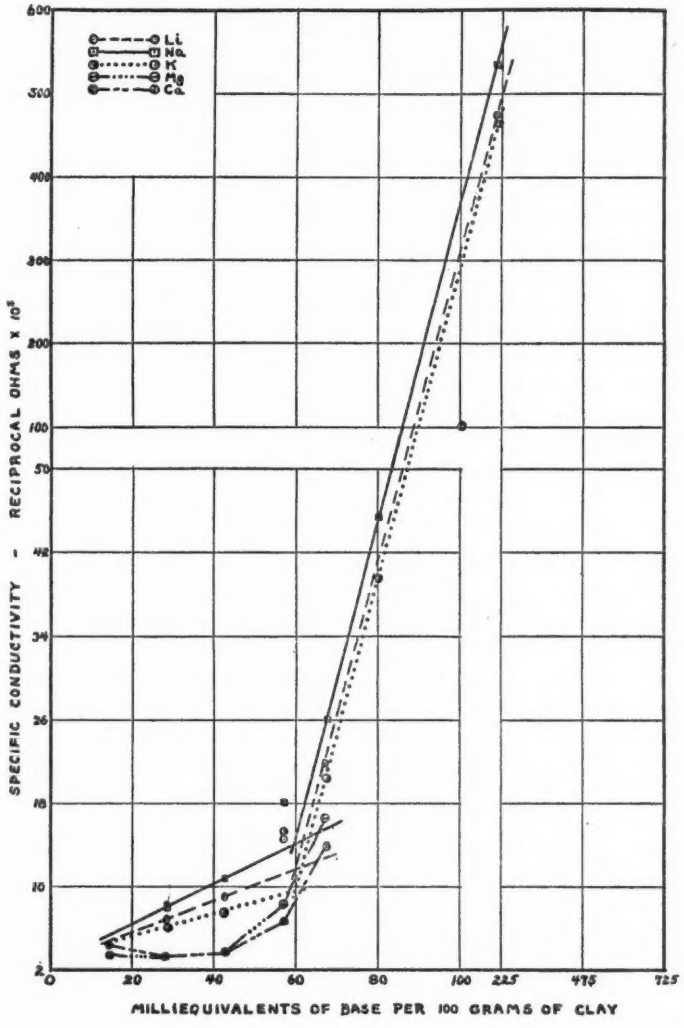

FIG. 2. SPECIFIC CONDUCTIVITY OF CLAYS CONTAINING DIFFERENT AMOUNTS OF BASES

indicating the point at which all of the exchangeable H ions have been replaced from the particles. The points above the Li-, Na-, and K-clay curves represent

hydrolysis effects, signifying that there has been an increase in the number of ions in solution. This increase is only apparent with the monovalent cations. The insolubility of the clay salts with the divalent ions causes a different type of curve. When a saturated clay is treated with an excess of a strong alkali there are some decomposition of the alumino-silicate complex and the formation of simpler silicates and aluminates. The divalent decomposition products are less soluble than the monovalent. Bradfield (7) has suggested that bases with divalent cations, because of these effects, are not suitable for the conductometric determination of the saturation capacity.

The conductivity curves of Li-, Na-, and K-clays exhibit an apparent discrepancy with regard to hydration, since the conductivity is greater according to the series: Na > Li > K. However, two different factors must be considered in these effects, the degree of dissociation of the different clays and the mobility of the ions resulting from this dissociation. The dissociation of these clays follows the order: Li > Na > K. There will be more Li ions in solution than Na and K ions. The Li ion has the lowest mobility because of its high hydration. The K ion has the greatest mobility. Therefore, the nature of the conductivity curves will be dependent not only upon the amount of a particular ion but also upon its mobility. In this way, the Li-clay possesses a conductivity intermediary berween that of the Na- and K-clays.

FLOCCULATION

The flocculation values for these clay sols, expressed as milliequivalents of base per 100 gm. of clay on the basis of a 2.3534 per cent by weight suspension, are as follows: Li = 536; Na = 536; K = 217; Ca = 67; Mg = 67.

These results distinctly show the effects of the valency and hydration of ions on the flocculation of colloidal clay. The flocculation value for the K ion is approximately one-half that for the highly hydrated Li and Na ions. Tuorila (42) observed that the minimum electrolyte requirement for a clay sol was about the same for LiCl and NaCl but that the amount of KCl necessary for flocculation was about two-thirds less. The divalent ions flocculate at a much lower concentration.

Bradfield (6) has definitely shown that there must be an excess of cations in the intermicellar liquid above the saturation point of the colloid in order to decrease the charge on the particle and produce flocculation. This excess depends upon the valency and hydration of the ions. This is confirmed by the results with this colloidal clay. The divalent cations flocculated the clay when the excess of these ions was about 17.5 per cent above the saturation point. This amount was 282 and 840 per cent above saturation with the K and the Li and Na ions, respectively. Hissink (23) reports that clay is in a flocculated condition when the absorbing complex is 95 per cent saturated with Ca. Gallay's (18) and de Sigmond's (14) results indicate that flocculation takes place either at the saturation point or slightly above it. This range will vary

with the method of determining the absorptive capacity, the nature of the clay, and the nature of the anion introduced into the system with the added Ca ion.

MIGRATION VELOCITY

The stability of a colloidal system is dependent upon the charge and hydration of the particles, which in turn depend upon the nature of the colloid. The charge on the particle is the sole factor determining the stability of lyophobic sols. Removal of the charge from the colloidal particles results in flocculation. Powis (35) has shown, however, that complete removal of the charge is not necessary to produce flocculation. A lowering of the electrokinetic potential to a certain value, which he calls the "critical potential," is sufficient to bring about flocculation.

The ion of opposite charge to that of the particle is responsible for this lowering of the potential. This indicates that the electrokinetic potential is due to the ions held on the surface of the particles. These ions may be absorbed by the particle or they may arise from the particle by surface dissociation.

The exchangeable cations form the outer layer of the particle. The charge will be greater as the hydration of these cations is larger, according to the ionic series: Li > Na > K > Rb > Cs; and Mg > Ca > Sr > Ba.

The electrokinetic potential of colloidal particles is greatly influenced by electrolytes. The curves giving the relation between charge and electrolyte concentration generally exhibit a maximum with the mono- and divalent ions at low concentrations, then decrease as the concentration of these ions increases. These relationships are fully discussed by Svedberg (37) and Kruyt (26). Tuorila (42) studied the effect of different electrolytes on the migration velocity of clay sols and found that this velocity was lowered according to the following electrolyte and cation series: LiCl < NaCl < KCl = $AgNO_3$ < CaCl < HCl; and $MgCl_2$ < $CaCl_2$ < $SrCl_2$ < $BaCl_2$.

There was a slight increase in these velocities with small additions of the monovalent chlorides, LiCl, NaCl, and KCl. The divalent chlorides and HCl caused an immediate decrease in the velocity of the particles. The clay suspensions, however, were not freed from exchangeable bases before being treated with the various electrolytes. Mattson (37) reports that the migration velocity of electrodialyzed clay and of bentonite increases when these colloids are saturated with Na, and decreases when Ca is the saturating ion. He finds that the electrokinetic potential reaches a maximum before 100 per cent saturation with Na. Anderson (1) observed that the colloids saturated with H ions have a lower potential than those saturated with Ca. However, his method of saturating his soils with the different cations probably accounts for this difference.

The migration velocity of the clay sols containing various amounts of exchangeable cations was determined ultramicroscopically by the method suggested by Tuorila (43). These results are given in table 1 and figure 3. The

cataphoresis curves show very markedly the effect of the valency of the cation on the charge of the clay particle. The effect of hydration is not strongly expressed. However, the lyotropic effect of the ions is present. The curves for the monovalent cations are characterized by an initial increase in the migration velocity up to a maximum, from which they fall off sharply to a more or less constant value as the concentration of ions in the system increases. This maximum point is reached at the saturation capacity of the colloid for bases, indicating that the maximum activity of the ions on the particle exerting their effect on the migration velocity is reached at this value. The sharp decrease

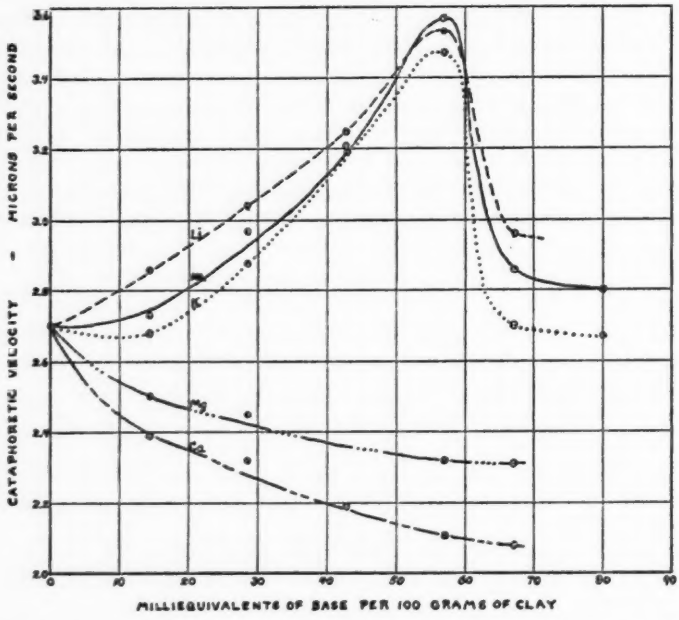

FIG. 3. MIGRATION VELOCITY OF CLAY PARTICLES AS AFFECTED BY THE AMOUNT AND NATURE OF EXCHANGEABLE CATIONS

in the velocities can be explained by considering the higher concentration of ions in solution as suppressing the effect of the ions on the particle. In other words, there is a repression of the ionization of the particular clay salts with a subsequent reduction of the number of "active ions" on the surface of the particle. This causes a sharp decrease in the charge on the particle.

The divalent cations cause a gradual decrease in the charge on the particles as the concentration of these ions increases. This effect appears to be more or less universal in cataphoretic phenomena. It is probably due to the low dissociation of the Ca- and Mg-clays. A smaller number of ions on the particle

as well as a lower activity of these ions should be expected to cause a decrease in the charge on the particle.

The critical potential for the Li-, Na-, and K-clays is 38.2, 36.6 and 34.0 millivolts, respectively. This value for the Ca- and Mg-clays is 26.5 and 29.4. The H-clay with a potential of 34.3 millivolts is very close to the critical value, since the H-saturated sol is nearly flocculated. Tuorila found the critical potential for his particular clay suspension to be 48 millivolts for the monovalent cations and 45 to 46 millivolts for the divalent. The critical potential undoubtedly varies with the chemical composition of the colloidal clay. For any particular clay, the critical value will depend upon the nature of the flocculating agent.

TABLE 2

Effect of exchangeable Ca and Na upon the size of particles in colloidal clay

MILLIEQUIVALENTS OF BASE PER 100 GM. OF CLAY	SIZE (RADIUS) OF PARTICLES	
	Ca	Na
	μμ	μμ
0	136	136
14.25	126	113
28.50	122	96
42.75	121	98*
57.00	130	96*
67.00	148	...
536.00	...	110

* All particles not visible in ultramicroscope.

SIZE OF PARTICLES

The size of particles of the clay sols containing different amounts of exchangeable Na and Ca ions was determined in the ultramicroscope in order to measure the effect of these ions on the dispersion of the H-aggregate. These results are shown in table 2.

The average radius of the H-aggregate was found to be 136 μμ. The replacement of the H ions from the particles resulted in a dispersion of the aggregate, since the average radius of the particles decreased. This decrease reached a minimum of 121μμ with the Ca-clays when the particle was about 75 per cent saturated with this ion. Beyond this point, the size of the particles increased, indicating a flocculating effect. The average radius of the Ca-aggregate was 148μμ. The Na ion caused a distinct change in the dispersion of the H-clay. The observed results seem to indicate that the maximum dispersion of this clay sol produces a particle having a radius of 96μμ. However, the ultramicroscopic observations do not show the magnitude of this dispersion, probably because many of the smaller particles were not seen. It was very evident

from the appearance and behavior of these suspensions that a much higher degree of dispersion was obtained.

RATE OF ULTRAFILTRATION

A large difference was observed in the rate of filtration of these sols. The Ca-clays filtered much more rapidly than the Na. This different rate in the filtration velocity indicated a large difference in the size of the pores in the two clays. As filtration proceeds, a layer of clay is deposited upon the collodion membrane and also serves as a membrane. The thickness of this clay mem-

TABLE 3

A comparison of the rate of ultrafiltration of Ca- and Na-clays under a pressure of 100 pounds to the square inch

TIME	VOLUME OF ULTRAFILTRATE		
	Distilled water	Ca-clay	Na-clay
minutes	*cc*	*cc.*	*cc.*
10	13.0	9.5	9.0
20	22.5	17.0	13.5
30	32.5	24.0	17.5
40	42.5	30.0	20.5
50	....	35.5	23.5
60	....	41.0	26.5
70	....	45.5	29.0
80	....	50.5	31.0
90	....	55.0	33.0
100	....	....	34.5
120	....	65.5	38.25
140	....	....	41.50
160	....	79.5	44.75
180	....	95.5	47.25
200	....	....	49.25
380	....	....	62.75
430	....	....	68.25
510	....	....	75.25

brane becomes greater as the volume of ultrafiltrate increases. The rate of filtration of two clay sols, 50 per cent saturated with Ca and Na ions, was determined in order to ascertain the relative differences in the size of pores of the clay membranes. These results are shown in table 3 and figure 4.

The rate of ultrafiltration of water under a pressure of 100 pounds to the square inch was observed to be constant, amounting to 0.0166 cc./sec. The rate of filtration of the Na-sol decreases markedly as the colloid is deposited and the clay membrane is formed. This decrease is not so pronounced with the Ca-sol. This indicates that the size of the pores in the Na-clay are much smaller than those in the Ca. The relative size of the pores in the Ca-clay was

8.3 times greater than in the Na-clay membrane as calculated from the formula suggested by Bjerrum and Manegold (4). The curves clearly show that the Ca ion produces a porous structure, undoubtedly due to the size and stability of the floccules formed.

VISCOSITY

Viscosity measurements have been rather extensively used for studying the properties of lyophilic colloids, even though most of the work has been more or less relative in character. It has been fairly well established that the viscosity of colloids is a function of the volume occupied by the disperse phase. This volume includes that of the particle and any water of hydration that may be associated with it. Emulsoid particles have a much larger "active volume"

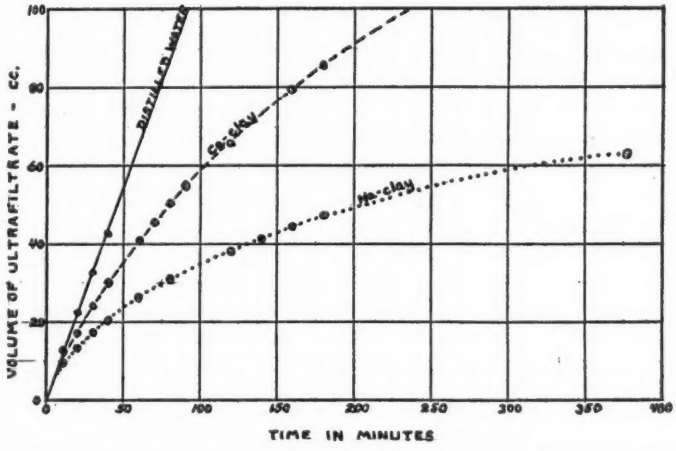

FIG. 4. EFFECT OF EXCHANGEABLE CALCIUM AND SODIUM UPON THE FILTRATION VELOCITY OF CLAYS

than that derived from the size of the particle itself. This suggests that they are strongly hydrated. The nature of this hydration may vary: water may be held as a film around the particle by the forces of adsorption; it may be adsorbed within the particle; or it may be the result of the hydration of the ions of an electrolyte associated with it. Agar possesses a high degree of hydration and therefore a high viscosity. Oden (32) has shown that the viscosity increased by increasing the degree of dispersion of his sulfur sol. This was undoubtedly due to water adsorbed on the increased surface of the smaller sulfur particles.

Numerous investigators (10, 17, 24, 29) have observed that the addition of small amounts of electrolytes to colloidal systems produces a sharp drop in their viscosity, depending upon the nature of the colloid and the type of electrolyte. These viscosity changes appear to follow a course similar to that of the electrokinetic potential of colloidal systems.

There have been several theories proposed as an explanation of the nature of this decrease in the viscosity of colloids. Kruyt (26) attributes this behavior of the system to an "electro-viscous effect." By this is meant that an electrical charge on the particles produces a certain viscosity as a result of an increase in the active volume of the dispersed phase. A removal of the charge on the particle results in a decrease in viscosity. This theory is based upon Smoluchowski's modification of the Einstein viscosity equation. The elctro-viscous effect has been confirmed by the experiments of Kruyt and de Jong (27), de Jong (11), Eggink (15), and Whitby and Jane (44).

Pauli (34), in discussing the colloid chemistry of the proteins, attributes their physico-chemical properties to their degree of ionization. Hydration of protein particles increases as ionization proceeds. This is concurrent with an increase in viscosity. Similar hypotheses are advanced by Lewis and Daniel (28) and Thomas and Frieden (38).

Wiegner (45) considers the hydration of ions as playing the important rôle in viscosity changes. Particles containing hydrated ions on their surfaces are voluminous and viscous in pure water. Those particles containing weakly hydrated ions around the primary particle have a low viscosity. His theory is supported by the data of Gallay (18), stating that the hydration of particles is dependent upon the nature of the ions in the exterior liquid and the nature of the adsorbed ions.

Viscosimetric determinations have been used by Wiegner (45), Gallay (18), and Demolon and Barbier (12) for studying the changes taking place in the coagulation of colloidal clay. Viscosity was found to increase during flocculation because of the hydration of the floccules. The viscosity of colloidal suspensions containing different ions adsorbed on the dispersed phase decreases in order of the decrease in hydration of the respective ions. Viscosity is greater according to the progression: $Li > Na > NH_4$ and $K > Rb > Cs$ for the monovalent ions, and $Mg > Ca > Ba$ for the divalent. Demolon and Barbier (12) observed that the permeability of coagulated clay increased with the concentration of electrolytes. A distinct correlation was found between viscosity and permeability up to a certain maximum viscosity.

The viscosity of these different clay suspensions was measured with a Washburn modification of the Ostwald type of viscosimeter. The experimental results are given in table 1, and figure 5. It is very evident that the monovalent and divalent cations exert entirely different effects upon the viscosity of these clays. These effects may be explained as representing two types of hydration changes.

Hydration of the system can be due either to a water film around the particle as produced by the absorption of highly hydrated ions, or to water held between particles in aggregate formation. In either case there is an increase in the total active volume of the dispersed phase, resulting in an increase in viscosity.

A careful study of the viscosity curves shows that both of these hydration effects occur with the monovalent ions. The H-saturated clay is not a mono-

dispersed system. It is composed of loosely bound, hydrated aggregates. The addition of 14.25 milliequivalents of a monovalent base produces a marked decrease in viscosity. This decrease is the greatest with the K ion and least with the Li ion. The difference between the Li, Na, and K ions is purely a lyotropic effect.

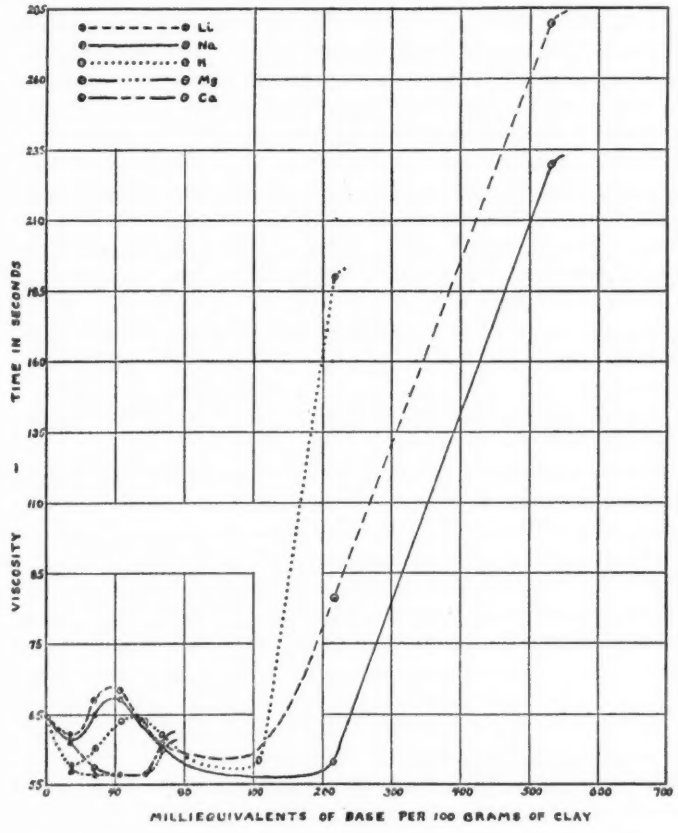

FIG. 5. VISCOSITY OF CLAY CONTAINING DIFFERENT AMOUNTS OF BASES

There are two opposing forces exerting their influence on the viscosity changes. Dispersion of the H-clay aggregate tends towards a decrease in the total volume of the dispersed phase and a decrease in viscosity. Hydration of the dispersed particles causes an increase in this volume and in viscosity. Therefore, the K ion, with the lowest hydration of the monovalent ions used, produces the least hydration of the particles, decreasing the viscosity the great-

est. The high hydration of the Li ion nearly counterbalances the effect of dispersion, inasmuch as the viscosity decreases slightly.

As the concentration of exchangeable monovalent cations becomes greater the viscosity increases to a maximum near the saturation capacity of the colloid for bases. From this point it rapidly decreases to a minimum, increasing again as flocculation begins. This initial increase represents an augmentation in hydration as the concentration of hydrated ions on the particle becomes greater. This maximum point represents the point of the largest hydration of the particle and corresponds fairly well to the point of maximum charge. The rapid decrease in viscosity is explained as being due to a repression of the ionization of the ions on the complex with a subsequent decrease in viscosity. A similar effect takes place in the migration velocity of the particles, as previously mentioned.

The potentiometric and conductometric results show that the number of ions in solution, free from the surface of the colloid, increases rapidly above 50 milliequivalents of base per 100 gm. of clay. This suggests that with a larger number of ions in solution, the concentration of ions on the particle exhibiting the property of hydration decreases. In other words, the Li-, Na-, and K-clays begin to exhibit effects analogous to the hydrolysis of salts of weak acids. These effects have also been suggested by Bradfield (5), and Breazeale and McGeorge (9).

The increase in the concentration of ions in solution causes a corresponding decrease in hydration and viscosity to a minimum. An increase in viscosity occurs at the point where slow coagulation begins. As aggregation proceeds, water is enmeshed between the particles and this hydration of the floccules cause an increase in viscosity. The viscosity of the flocculated clays is greatest according to the lyotropic series: Li > Na > K.

The divalent ions exhibit a different type of curve. There is a continuous decrease in viscosity until about 60 milliequivalents of Ca or Mg per 100 gm. of clay have been added. At this point there is an increase in viscosity because of coagulation. This continuous decrease in viscosity signifies a lowering of the hydration of the particles with respect to that of the original H-saturated aggregates. This indicates that the Ca ion has caused at least a partial dispersion of the original aggregate. This is confirmed by ultramicroscopic counts. The radius of the H-aggregate was found to be 136 $\mu\mu$. This size decreases to 121 $\mu\mu$ as the concentration of Ca ions on the complex increases. The Ca-aggregate at the point of flocculation has an average radius of 148 $\mu\mu$. These effects are paralleled by a decrease in the charge on the particle.

If the addition of small amounts of Ca ions to the H-clay maintained the original aggregate, viscosity would not be expected to diminish materially. Neither should there be a decrease in the size of the particles or aggregates. The data appear to indicate that the replacement of H ions on the particle may proceed in two ways. One divalent cation either replaces two H ions from the same particle or one H ion from each of two adjacant particles. In the latter case, a doublet is formed. The divalent cation does not carry water

of hydration to the particle and the total volume decreases, causing a diminution of viscosity. This connecting ion ceases to exert any influence on the system. Consequently, there is also a decrease in the electrokinetic potential, since a larger particle is formed with a smaller number of ions exerting their influence on the charge. Mattson (30), Ehrenberg (16), and Hager (22) advance similar hypotheses. However, they add that the Ca ion joins to one OH ion from each of two particles. Irrespective of the nature of this linkage, it appears logical to expect that a divalent ion can replace ions from two adjacent particles, especially when the particles are originally in contact in the form of loose aggregates. The effect of the Mg and Ca ions is practically the same. Hydration effects are not very evident.

It is very interesting to note that the sols containing 67 milliequivalents of Ca and Li have the same viscosity. However, there is a distinct difference in the type of viscosity. The Li-clay owes its viscosity to water of hydration produced by Li ions on the individual particles. The Ca-sol possesses a viscosity due to water enmeshed between particles during aggregation.

The viscosity of the coagulated sols is greatest according to the ionic series: Li > Na > K > H > Ca and Mg. Gallay (18) observed that the Ca-soil possessed the lowest viscosity. Ultramicroscopic observations show that the H-aggregate is smaller than that of Ca. These two facts are of prime importance from the standpoint of structure. The higher viscosity of the H-aggregate indicates a hydrated, loosely bound system which is semi-reversible into the dispersed state. The Ca- and Mg-aggregates are more stable, less hydrated, and therefore less viscous. Demolon and Barbier (12) found that salts with a high flocculating power gave rise to large aggregates having a distinct rigidity and maximum permeability. Na salts produced small, loose aggregates with a minimum permeability. Therefore, soils saturated with Ca and Mg would have a structure favorable for the movement of air and water. This structure would be fairly stable and not subject to fluctuations brought about by seasonal changes.

DISCUSSION

The physico-chemical behavior of this colloidal clay appears to be a function of the "active ions" on the surface of the colloid. The "active ions" are those ions which are dissociated from the particle. The non-ionized fraction of the total number of ions associated with the particle are considered as having no direct effect upon the properties of the system.

The monovalent ions exert varied effects upon the properties of the clay, depending upon the amount and nature of the ion. The divalent ions always have a diminishing effect. The maximum activity of the monovalent ions takes place near the point of saturation of the colloid with cations. This value appears to be a function of the hydration of the ions. The decrease in viscosity and charge beyond the point of saturation of the colloid is due to a repression of the number of "active ions" on the particle.

The results of this investigation upon the changes in the viscosity and charge of colloidal clay as produced by increasing quantities of cations indicate that the theories of Kruyt, Pauli, and Wiegner are not so widely different. The viscosity and migration velocity curves confirm the results of Kruyt. A definite electro-viscous effect is exhibited as the concentration of cations increases above the saturation capacity of the colloid. From Pauli's point of view, this can be explained as being due to a decrease in ionization. Or, as suggested by Wiegner, there is a decrease in the hydration of the colloid. These data clearly point out the possibility of a more unified interpretation of the behavior of colloidal systems.

There appears to be no direct relation between the relative amounts of any particular cation on the colloid and the properties of the clay when compared with other ions. In other words, the properties of the system are not directly proportional to the degree of substitution of any one base for another. This is especially true in comparing the effects of the monovalent and divalent ions. The relationships existing between the monovalent ions are somewhat similar. Mattson's results justify the same conclusion. Anderson, however, states that there tends to be a direct relation between the properties of colloidal clay and the degree of substitution of the various bases. However, the effect of the Cl ions in his clays and his interpolation between the existing data probably account for these differences.

The nature of the effects on the properties of this clay brought about by the Ca ion is of major importance in soil structure problems. It is commonly believed that the granulation of a soil is concurrent with good structure. All attempts towards improving the physical condition of a heavy soil are based on the production of a granular structure. The Ca ion has always been used as the agent for producing this granulation. These results show that the Ca-aggregate is rather large, having a low viscosity. It is fairly well established that the Ca-aggregate is rather stable. This fact has been observed in a previous study. The H-aggregate is smaller and slightly more viscous, indicating a higher degree of hydration and lower stability. The aggregates produced by the monovalent ions are extremely viscous. The stability of the Ca-aggregate is of prime importance in the maintenance of any particular type of structure. Its stability is related to its low hydration, to its low potential, and probably to the union of particles as previously suggested.

Aggregation of this colloidal clay takes place when the concentration of Ca is slightly above the saturation point of the colloid. Conductivity data show an increase in the concentration of ions at this point, suggesting that the colloid must be saturated with Ca in order to maintain the maximum state of aggregation. As exchangeable Ca is replaced by the H ion, the complex breaks down into a higher degree of dispersion, producing a structure that is more or less reversible, depending upon seasonal conditions. The fact that an excess of Ca ions above the saturation capacity of the colloid is required to produce flocculation is very important from the standpoint of an intelligent liming program on acid clay soils.

SUMMARY

1. Electrodialyzed Putnam clay was saturated to different degrees by titrating the H-clay with the hydroxides of Li, Na, K, Mg, and Ca.

2. The saturation capacity of this clay was found to be 57 milliequivalents per 100 gm. of clay.

3. The reaction of clay sols containing various amounts of the different cations was greatest according to the lyotropic series of cations: Li > Na > K > Mg > Ca > H.

4. The specific conductivity followed the order: Na > Li > K > Mg > Ca.

5. The flocculation values of the Li-, Na-, K-, Mg-, and Ca-sols were 536, 536, 217, 67, and 67 milliequivalents of base per 100 gm. of clay, respectively, with a 2.3534 per cent by weight suspension.

6. The monovalent cations increased the charge on the particles to a maximum at the saturation capacity of the colloid. The charge decreased as the concentration of ions increased beyond this point. Divalent cations decreased the charge.

7. The average radius of the H-aggregates was 136 $\mu\mu$; that of the Ca-aggregates was 148. The size of the pores in the Ca-clay were much larger than those in the Na-clay.

8. Small amounts of monovalent cations produced a decrease in viscosity. This was followed by an increase to a maximum near the saturation point of the clay. Here a rapid decrease occurred, followed by an increase when flocculation took place. The divalent cations decreased the viscosity to the point of flocculation where it increased sharply. The hydration and viscosity of the clay aggregates were greatest according to the order: Li > Na > K > H > Ca > Mg.

9. The changes in the physico-chemical properties of these clay sols are explained as being a function of the number of "active ions" on the particle.

10. The size, stability, and low hydration of the Ca- and Mg- aggregates are considered as important factors for producing and maintaining a good soil structure.

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REMOVAL OF IONS FROM SOLUTIONS OF CALCIUM DIHYDROGEN PHOSPHATE BY TREATMENT WITH HYDROUS GELS OF ALUMINA, SILICA, AND THEIR MIXTURES

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Received for publication September 4, 1929

Much attention is being directed to the soil factors governing the supply of phosphate to the growing plants, and important work on this subject has recently been done by Wrangell (21) and by Parker and Tidmore (16). Apparently, however, no illuminating theoretical treatment of the subject is possible unless complete experimental data are available on the absorption of the ions from solutions of varying concentrations of calcium dihydrogen phosphate by the inorganic and organic gels that constitute the soil colloids separately and in mixtures of known composition.

In this paper experimental results will be presented on the ionic composition of the solutions obtained after prolonged shaking of solutions of calcium dihydrogen phosphate with gels of alumina, silica, and their mixtures. The natural inorganic colloids of the soil are composed of the completely broken down products of weathering, which are mainly colloidal silica, alumina, and ferric hydroxide. According to Bradfield (3), however, this natural inorganic colloid mixture differs considerably in cataphoretic behavior and buffer action from a synthetic mixture of colloidal silica, alumina, and ferric hydroxide. Mattson (12) has recently studied the cataphoretic behavior and base exchange capacities of synthetic alumino-silicates, and he finds that these are of the same order of magnitude as those of natural gels. His experiments on the reaction between alumino-silicates and solutions of calcium hydroxide "speak strongly in support of the theory that both the ions of $Ca(OH)_2$ are adsorbed and against the theory of neutralization and existence of alumino-silicic acids." We shall not therefore be far wrong when we proceed with the assumption, which now finds favor with the majority of investigators, that the inorganic colloidal soil materials are adsorption compounds of indefinite composition formed by the mutual precipitation of colloidal hydroxides of opposite charges, and that synthetic mixtures of these colloids have properties which are analogous to those of the natural material. Wiley and Gordon (20) have studied the absorption of ions from various salt solutions by gels of silica and alumina. The relation of their experimental results to those obtained in this investigation will be discussed later. They have not made clear how they freed the solution from the fine particles of the gels; our experience shows that for this purpose satis-

factory results are obtained only when collodion sacs are used for dialysis, as will be described in the following pages.

EXPERIMENTAL

Preparation of gels

Alumina was prepared from a solution of aluminum nitrate by the addition of ammonium chloride and ammonium hydroxide. Silica was prepared by the hydrolysis of silicon tetrachloride and final precipitation with ammonium hydroxide. Alumina-silica mixture was prepared: first, by the addition of varying amounts of aluminum nitrate and sodium silicate solutions; and second, by the hydrolysis of silicon tetrachloride followed by the addition of aluminum nitrate solution. The mixtures were then neutralized with dilute ammonium hydroxide or dilute hydrochloric acid, as the case may be, and finally precipitated by the addition of ammonium chloride and ammonium hydroxide.

In all these cases the gel was first washed seven or eight times with distilled water by decantation and then dialyzed for about two months. The gel was then filtered through a Buchner funnel, washed with conductivity water, and then kept in a closed vessel over water. It was observed that the alumina-silica mixtures of the same composition from both the preparations gave approximately the same result when treated with phosphate solution.

The composition of the gels, amount of moisture, alumina as Al_2O_3, and silica as SiO_2 were determined in every sample. These have been expressed as per cent hydration, per cent Al_2O_3, and per cent SiO_2 respectively.[1]

Obtaining solutions in equilibrium with the gels[2]

Some preliminary experiments were made to determine the time required for an equilibrium to be attained when a calcium dihydrogen phosphate solution was dialyzed through a collodion sac. The method consisted in putting about 30 cc. of phosphate solution inside a collodion sac which was immersed in 60 cc. of water contained in a wide beaker, the level of water inside and out being almost the same. The same volume of solution from inside and outside was examined for phosphate after different intervals of time. It was observed that for an equilibrium to be attained, i.e. for the same amount of phosphate to be obtained in the same volume of solution from inside and out, the minimum time required was 12 hours. Even after 11 hours a marked difference in the amount of phosphate in the inside and outside solution was observed.

Five grams of hydrated gel was accurately weighed off in a series of conical flasks. Varying quantities of calcium dihydrogen phosphate [$CaH_4(PO_4)_2 \cdot 2H_2O$] solution were added. The volumes of the contents were made the same by the addition of water. The conical flasks were shaken for about four hours

[1] In estimating Al_2O_3 and SiO_2, the processes given in *Jour. Amer. Chem. Soc.* (1916) 38: 1282, and "Quantitative chemical analysis" by Treadwell and Hall, respectively, have been followed. Moisture was determined by igniting a part of each sample.

[2] Parker's (15) method, with certain modifications, was adopted.

in a shaking machine. The contents were then quantitatively removed to a series of collodion sacs, each being immersed in a known volume of water outside so that the levels of water inside and outside were almost the same in all these cases. Glass stirrers run by motor were fitted inside the collodion sacs, so that the contents of the sacs were stirred uniformly during the whole time of dialysis. After about 16 to 20 hours, a portion of outer solution from each was removed for the estimation of phosphate. From this the total amount of phosphate present in the solution was calculated as P_2O_5. The difference between this and the total amount used gave the amount of P_2O_5 adsorbed.

Standard phosphate solution was prepared by dissolving 13.3135 gm. of calcium acid phosphate and making it up to 500 cc. This gave a solution containing 1.5 gm. of P_2O_5 to 100 cc. Different phosphate standards were prepared by diluting this solution to required volumes.

Throughout the experiments, conductivity water was always used.

The pH value of the remaining outer solution was determined electrometrically.

Estimation of phosphate and calcium

The method for the estimation of phosphate was that of Deniges (5) recently modified by Parker (15).

The method for the estimation of calcium was similar to that given by Kuttner and Cohen (10), the calcium being precipitated as phosphate and the phosphorus estimated colorimetrically.

Determination of pH

Colorimetric determination of pH with the standard buffer solution was tried, but was found to be unsatisfactory for accurate determinations.

Hence the electrometric method of measuring hydrogen-ion concentration was used. The procedure given by Clarks (4) has been scrupulously followed.

EXPERIMENTAL RESULTS

The experimental data are given in tables 1 through 9. Column 4 gives the concentration of P_2O_5 in gram molecules in each liter of solution. In calculating the quantity of solvent, the water present in the hydrated gel has been taken into account. In column 9 is given the concentration of hydrogen ions in $CaH_4(PO_4)_2$ solution before treatment with the gel; column 11 gives the concentration of hydrogen ions in the solution after adsorption equilibrium has been established. Columns 12, 13 and 14 give the concentrations in gram ions of H_2PO_4', HPO_4'', and H_3PO_4, respectively, in the final solutions. These values have been obtained from the following equations:

$$\Sigma\,(H_2PO_4') + (HPO_4'') + H_3PO_4 = 2 \text{ conc. of } P_2O_5 \text{ in mols per liter} \ldots (A) \ldots \text{(column 4)}$$

$$\frac{(H)\ (H_2PO_4')}{H_3PO_4} = 1.1 \times 10^{-2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (B)$$

$$\frac{(H)\ (HPO_4'')}{H_2PO_4'} = 2 \times 10^{-7} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (C)$$

TABLE 1

Ionic composition of solution obtained after prolonged shaking with solutions of calcium dihydrogen phosphate, in varying concentrations, with pure silica gel
(SiO_2 = 0.4373 gm.)

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)
Total gm. mol. P_2O_5 used = total gm. mol. Ca used	Total gm. mol. P_2O_5 adsorbed	Total gm. mol. P_2O_5 in soln.	Gm. mol. P_2O_5 in soln. per liter	Total gm. mol. Ca adsorbed	Total gm. mol. Ca in soln.	Gm. mol. Ca in soln. per liter	Conc. of univalent ions obtained by exchange	Initial C_H	Final pH	Final C_H	H_2PO_4'	HPO_4''	H_3PO_4	Gm. P_2O_5 adsorbed per gm. total adsorbent	Gm. mol. P_2O_5 adsorbed per gm. mol. Al_2O_3 considering SiO_2 absent	Gm. Ca adsorbed per gm. total adsorbent	Gm. mol. Ca adsorbed per gm. mol. Al_2O_3 considering SiO_2 absent
0.003169	0.000415	0.002754	0.0291	.....	.....	.....		4.467×10^{-3}	3.05	0.881×10^{-3}	.....		.....	0.1349	.....	.....	.....
0.002640	0.000359	0.002281	0.0241	.....	.....	.....		3.981×10^{-3}	3.08	0.832×10^{-3}	.....		.....	0.1167	.....	.....	.....
0.002113	0.000297	0.001815	0.0191	0.0004125	0.0017	0.01797		3.236×10^{-3}	3.153	0.703×10^{-3}	0.036		0.0022	0.0965	.....	0.03773	.....
0.001585	0.000232	0.001352	0.0142	.....	.....	.....		2.512×10^{-3}	3.20	0.631×10^{-3}	0.0269		0.0015	0.0754	.....	.....	.....
0.001056	0.000162	0.000894	0.0094	0.0002263	0.00083	0.008774	Negligible	1.585×10^{-3}	3.38	0.417×10^{-3}	0.0177	Nil	0.0007	0.0526	.....	0.0207	.....
0.000528	0.000077	0.000450	0.00476	.....	.....	.....		0.5012×10^{-3}	3.75	0.178×10^{-3}	0.00936		0.00016	0.0252	.....	0.0138	.....
0.0002113	0.000039	0.000172	0.0018	.....	.....	.....		.....	.....	.....	.....		.....	0.0128	.....	.....	.....
0.000106	0.000015	0.000091	0.00096	.....	.....	.....		.....	.....	.....	.....		.....	0.0058	.....	.....	.....

TABLE 2

Ionic composition of solution obtained after prolonged shaking with solutions of calcium dihydrogen phosphate, in varying concentrations, with $Al_2O_3 + SiO_2$ gel
($Al_2O_3 + SiO_2$ = 0.25 gm.; Al_2O_3 = 0.026 gm., or 10.4 per cent; SiO_2 = 0.224 gm., or 89.6 per cent)

0.003169	0.000443	0.002725	0.0287	.....	.....	.....	.....	4.217×10^{-3}	3.58	0.263×10^{-3}	0.05736	0.00004		0.252	1.738	.....	.....
0.002640	0.000404	0.002235	0.0235	.....	.....	.....	.....	3.758×10^{-3}	3.68	0.209×10^{-3}	0.04697	0.00003		0.230	1.584	.....	.....
0.002113	0.000362	0.001750	0.0184	0.0005875	0.001525	0.01610	0.004505	3.162×10^{-3}	3.87	0.135×10^{-3}	0.03676	0.00004	Nil	0.205	1.420	0.094	2.304
0.001585	0.000316	0.001267	0.0130	.....	.....	.....	.....	2.307×10^{-3}	4.19	0.0646×10^{-3}	0.02592	0.00008		0.180	1.240	.....	.....
0.001056	0.000239	0.000816	0.0086	0.0003288	0.0007275	0.007683	0.00195	1.259×10^{-3}	4.62	0.0239×10^{-3}	0.1706	0.00014		0.136	0.937	0.0526	1.29
0.000528	0.000119	0.000407	0.0042	0.0001658	0.0003625	0.003826	0.0009554	0.4217×10^{-3}	5.12	0.00759×10^{-3}	0.008185	0.000215		0.068	0.4667	0.0265	0.6503

TABLE 3

Ionic composition of solution obtained after prolonged shaking with solutions of calcium dihydrogen phosphate, in varying concentrations, with $Al_2O_3 + SiO_2$ gel

($Al_2O_3 + SiO_2 = 0.56$ gm.; $Al_2O_3 = 0.1516$ gm., or 28.9 per cent; $SiO_2 = 0.3986$ gm., or 71.1 per cent)

0.003169	0.002221	0.000947	0.01003	.....	.....	.....	.....	1.585×10^{-3}	5.566	2.716×10^{-6}	0.01868	0.00138	Nil	0.5633	1.49	.....	.....
0.002640	0.001927	0.000713	0.00755	.....	.....	.....	.....	0.8913×10^{-3}	5.735	1.832×10^{-6}	0.01361	0.00149		0.4888	1.293	.....	.....
0.002113	0.001636	0.000475	0.00503	0.001538	0.000575	0.006091	.....	0.5164×10^{-3}	6.03	0.933×10^{-6}	0.00828	0.00178		0.4150	1.098	0.1098	1.032
0.001056	0.000868	0.000187	0.00198	0.0008895	0.0001675	0.001774	0.002278	0.1905×10^{-3}	6.65	0.224×10^{-6}	0.00209	0.00187		0.2202	0.5825	0.0635	0.597
0.000528	0.000428	0.0001001	0.00106	0.0004108	0.0001175	0.001245	0.001649	0.1156×10^{-3}	6.853	0.1403×10^{-6}	0.000101	0.00202		0.1085	0.2872	0.0293	0.276

TABLE 4

Ionic composition of solution obtained after prolonged shaking with solutions of calcium dihydrogen phosphate, in varying concentrations, with $Al_2O_3 + SiO_2$ gel

($Al_2O_3 + SiO_2 = 0.4007$ gm.; $Al_2O_3 = 0.2083$ gm., or 50.87 per cent; $SiO_2 = 0.1924$ gm., or 49.13 per cent)

0.003169	0.002244	0.0009253	0.009772	.....	.....	.....	.....	1.496×10^{-3}	5.34	4.571×10^{-6}	0.0187	0.00082	Nil	0.7949	1.100	.....	.....
0.002113	0.001684	0.000429	0.004533	.....	.....	.....	.....	0.4603×10^{-3}	5.70	1.995×10^{-6}	0.00824	0.000822		0.5967	0.825	.....	.....
0.001056	0.0009187	0.0001375	0.001452	.....	.....	.....	.....	0.4603×10^{-3}	6.48	0.331×10^{-6}	0.00181	0.001093		0.3256	0.450	.....	.....
0.0006338	0.0005314	0.0001024	0.001082	.....	.....	.....	.....	0.1349×10^{-3}	7.03	0.0933×10^{-6}	0.000689	0.001476		0.1882	0.261	.....	.....
0.0003169	0.0002738	0.0000430	0.000454	.....	.....	.....	.....	0.0794×10^{-3}	7.72	0.0191×10^{-6}	0.0000789	0.00829		0.0970	0.134	.....	.....
0.000169	0.0001274	0.0000417	0.000440	.....	.....	.....	.....	.....	.....	.....	0.0000288	0.000361		.....	0.0625	.....	.....

TABLE 5

Ionic composition of solution obtained after prolonged shaking with solutions of calcium dihydrogen phosphate, in varying concentrations, with $Al_2O_3 + SiO_2$ gel

($Al_2O_3 + SiO_2 = 0.3135$ gm.; $Al_2O_3 = 0.199$ gm., or 63.48 per cent; $SiO_2 = 0.1145$ gm., or 36.48 per cent)

0.003169	0.002807	0.0003621	0.003823	0.002767	0.000403	0.004256	.....	0.355×10^{-3}	5.6	2.512×10^{-6}	0.00708	0.000564	Nil	1.272	1.440	0.3531	1.419
0.002640	0.002397	0.0002439	0.002575	0.002396	0.000245	0.002587	0.000446	0.231×10^{-3}	5.7	1.995×10^{-6}	0.00468	0.00047		1.086	1.230	0.3058	1.228
0.002113	0.001986	0.0001267	0.001339	0.001975	0.000140	0.001479	.....	0.133×10^{-3}	5.87	1.349×10^{-6}	0.00233	0.000340		0.899	1.019	0.2520	1.013
0.001585	0.001553	0.0000312	0.0003293	0.001555	0.000030	0.0003168	0.0002244	0.0708×10^{-3}	6.18	0.661×10^{-6}	0.00046	0.000199		0.704	0.796	0.1985	0.798
0.001056	0.001052	0.00000508	0.00005359	0.001049	0.0000066	0.0000697	.....	0.0603×10^{-3}	6.67	0.214×10^{-6}	0.0000055	0.000052		0.476	0.539	.....	0.538
0.000528	0.0005269	0.000001302	0.00001375	.....	.....	.....	.....	.....	7.3	.....	.....	.....		0.239	0.270	.....	.....

TABLE 6

Ionic composition of solution obtained after prolonged shaking with solutions of calcium dihydrogen phosphate, in varying concentrations, with $Al_2O_3 + SiO_2$ gel

($Al_2O_3 + SiO_2$ = 0.226 gm.; Al_2O_3 = 0.156 gm., or 69 per cent; SiO_2 = 0.07 gm., or 31 per cent)

(1) Total gm. mol. P_2O_5 used = total gm. mol. Ca used	(2) Total gm. mol. P_2O_5 adsorbed	(3) Total gm. mol. P_2O_5 in soln.	(4) Gm. mol. P_2O_5 in soln. per liter	(5) Total gm. mol. Ca adsorbed	(6) Total gm. mol. Ca in soln.	(7) Gm. mol. Ca in soln. per liter	(8) Conc. of univalent ions obtained by exchange	(9) Initial C_H	(10) Final pH	(11) Final C_H	(12) H_2PO_4'	(13) HPO_4''	(14) H_3PO_4	(15) Gm. P_2O_5 adsorbed per gm. total adsorbent	(16) Gm. mol. P_2O_5 adsorbed per gm. mol. Al_2O_3 considering SiO_2 absent	(17) Gm. Ca adsorbed per gm. total adsorbent	(18) Gm. mol. Ca adsorbed per gm. mol. Al_2O_3 considering SiO_2 absent
0.003169	0.003163	0.000005169	0.00005459	.....	.....	.....	.....	0.0603×10^{-3}	6.4	0.398×10^{-6}	0.0000726	0.0000365		1.988	2.067	.....	.....
0.002640	0.002637	0.000003752	0.00003962	.....	.....	.....	.....	.....	6.54	.....	.....	.....	Nil	1.657	1.724	.....	.....
0.002113	0.002110	0.000002482	0.00002621	.....	.....	.....	.....	.....	6.9	.....	.....	.....		1.326	1.379	.....	.....
0.001586	0.001579	0.000001234	0.00001303	.....	.....	.....	.....	.....	7.57	.....	.....	.....		0.995	1.032	.....	.....

TABLE 7

Ionic composition of solution obtained after prolonged shaking with solutions of calcium dihydrogen phosphate, in varying concentrations, with $Al_2O_3 + SiO_2$ gel

($Al_2O_3 + SiO_2$ = 0.34 gm.; Al_2O_3 = 0.266 gm., or 78.3 per cent; SiO_2 = 0.074 gm., or 21.7 per cent)

0.003169	0.00303	0.000139	0.00146	.....	.....	.....	.....	0.1413×10^{-3}	5.82	0.1514×10^{-6}	0.002579	0.000341		1.30	1.16	.....	.....
0.002640	0.002527	0.000113	0.00123	.....	.....	.....	.....	0.1318×10^{-3}	5.98	0.1047×10^{-6}	0.002061	0.00040		1.06	0.97	.....	.....
0.002113	0.002026	0.000087	0.00091	.....	.....	.....	.....	0.07943×10^{-3}	6.15	0.07079×10^{-6}	0.001419	0.000401	Nil	0.846	0.780	.....	.....
0.001056	0.00101	0.000046	0.000484	.....	.....	.....	.....	0.07079×10^{-3}	6.64	0.02291×10^{-6}	0.0005166	0.00045		0.422	0.400	.....	.....
0.000528	0.004907	0.0000373	0.000392	.....	.....	.....	.....	0.05495×10^{-3}	7.10	0.00794×10^{-6}	0.000223	0.000561		0.205	0.191	.....	.....

TABLE 8

Ionic composition of solution obtained after prolonged shaking with solutions of calcium dihydrogen phosphate, in varying concentrations, with $Al_2O_3 + SiO_2$ gel

($Al_2O_3 + SiO_2 = 0.372$ gm.; $Al_2O_3 = 0.3263$ gm., or 87.7 per cent; $SiO_2 = 0.0457$ gm., or 12.3 per cent)

0.003169	0.00236	0.000809	0.00856	.....	.....	.....	.....	1.259×10^{-3}	5.41	0.3859×10^{-5}	0.01628	0.00084		0.90	0.738	.....	.....
0.002640	0.00205	0.00059	0.00614	.....	.....	.....	.....	0.7079×10^{-3}	5.60	0.2512×10^{-5}	0.01137	0.00091		0.782	0.640	.....	.....
0.002113	0.0017	0.000413	0.00437	.....	.....	.....	.....	0.4786×10^{-3}	5.94	0.1148×10^{-5}	0.007444	0.001296	Nil	0.65	0.531	.....	.....
0.001585	0.00131	0.000275	0.00291	.....	.....	.....	.....	0.2884×10^{-3}	6.42	0.03802×10^{-5}	0.003815	0.002005		0.50	0.41	.....	.....
0.001056	0.000927	0.000129	0.001365	.....	.....	.....	.....	0.1349×10^{-3}	6.92	0.01202×10^{-5}	0.001025	0.001705		0.354	0.29	.....	.....

TABLE 9

Ionic composition of solution obtained after prolonged shaking with solutions of calcium dihydrogen phosphate, in varying concentrations with pure alumina gel

($Al_2O_3 = 0.403$ gm.)

0.003169	0.00136	0.0018	0.0190	.....	.....	.....	.....	3.236×10^{-3}	5.75	1.778×10^{-6}	0.03417	0.00384		0.483	0.3443	.....	.....
0.002640	0.00121	0.00142	0.0149	.....	.....	.....	.....	2.692×10^{-3}	5.86	1.380×10^{-6}	0.0260	0.00377		0.427	0.3063	.....	.....
0.002113	0.00111	0.00099	0.0104	0.001035	0.001078	0.01140	0.00234	1.778×10^{-3}	6.12	0.759×10^{-6}	0.0165	0.00434		0.392	0.2809	0.1028	0.2620
0.001585	0.00095	0.000634	0.0067	0.0009398	0.000645	0.006819	0.004518	0.794×10^{-3}	6.44	0.363×10^{-6}	0.00864	0.00476	Nil	0.335	0.2405	0.0933	0.2380
0.001056	0.00077	0.000284	0.0030	.....	.....	.....	.....	0.282×10^{-3}	6.75	0.178×10^{-6}	0.00283	0.00318		0.272	0.1949	.....	.....
0.000528	0.00043	0.000094	0.00099	0.0004363	0.000092	0.0009725	0.001479	0.100×10^{-3}	7.13	0.074×10^{-6}	0.000536	0.00144		0.153	0.1088	0.0433	0.1105

Equations (*B*) and (*C*) are obtained from experimental data of Abbot and Bray (1). H′ was determined by actual experiments in each case. The three unknown quantities H_3PO_4', H_2PO_4' and HPO_4'' can be calculated from the three equations. In column 8 are given the differences, $\Sigma 2\,(Ca'') + (H') - \Sigma'(H_2PO_4') + 2\,(HPO_4'')$. This value is always positive and is presumably due to univalent positive ions obtained by base exchange, as the possibility of aluminum existing in the ionic state between pH 4.5 and pH 8.5 is completely excluded by the experimental observation of numerous investigators whose works have been summarized by Hardy (6). It is not possible to state exactly what these univalent ions are; it is very possible that, since ammonia with an excess of ammonium chloride was used for the final precipitation of the gels, even after two months continuous dialysis some of the NH_4 ions would still be retained in the gel by adsorption, and these are replaced in the solution when the gel is shaken with $CaH_4(PO_4)_2$ solution.

DISCUSSION OF RESULTS

We shall first consider the adsorption of ions by hydrated silica. Gordon (19) has observed small positive adsorption of Ca ion by silica gel, when the pH is 4 and above; for phosphate ion he has always found positive adsorption.

It is suggested that when solutions of calcium dihydrogen phosphate are treated with silica gel, the following chemical reaction happens:

$$H_2SiO_3 + CaH_4\,(PO_4)_2 = CaSiO_3 + 2\,H_3PO_4$$

But according to Kohlrausche (9) and Kahlenberg and Lincoln (8) silicates of the general formula M_2SiO_3 and $MHSiO_3$ are almost completely hydrolytically dissociated when 1 gram mol is contained in 48 liters. Bogue (2) has shown that though the OH- ion concentrations of silicate solutions were not as large as those suggested by Kahlenberg, the pH values of silicate solutions in his experiments also were never less then 10.5. The value of the dissociation constant of silicic acid was found to vary between 13×10^{-9} and 5×10^{-12}, depending on the composition of the sodium silicate solutions used. This observation has also been confirmed by Harman (7). In our solutions (table 1), the pH values were never greater than 3.75, and it is therefore obvious that, under such conditions, $CaSiO_3$, even if formed, will undergo complete hydrolytic dissociation.

It will be seen from column 8 that the positive ion obtained by base exchange is negligible. The solutions contain only H_3PO_4, Ca, H, and H_2PO_4 ions.

The removal of Ca and H_2PO_4 ions in almost equivalent proportions can be explained on the hypothesis that silica gel adsorbs Ca ions by valency forces [primary adsorption of Mukherjee (14)], and the resulting electro-positive gel removes H_2PO_4 ions from the solution by forces of electrical attraction.

We shall next consider the adsorption of ions by pure aluminum hydroxide gel (table 9). Here the magnitude of adsorption is very large compared with that of the silica gel, and the pH values of the solutions after treatment with

the gel increase from 3 and 4 to 6 and 7. Such marked changes may lead us to expect that chemical reaction here may be the determining factor. We may, for example, assume a reaction of the type:

$$Al(OH)_3 + CaH_4(PO_4)_2 = \underset{\text{insoluble}}{CaHPO_4} + \underset{\text{soluble}}{AlPO_4} + 3H_2O$$

This at once explains the acid neutralizing action of this gel and also the removal of Ca and P_2O_5 in equivalent amounts and in considerable quantities from the solutions.

There is one factor, however, which apparently negatives this possibility. If $CaHPO_4$ were present as an insoluble solid phase in the system, then the law of mass action should apply and the product of the concentration of Ca and HPO_4 in the solution must be constant. The solubility of $CaHPO_4$ is given (18) as 0.136 gm. a liter. The solubility product roughly comes to 0.000001. The product of the concentrations of Ca and HPO_4 given, respectively, in columns 7 and 13 (table 9), however, does not give values which are even approximately constant. It appears, therefore, that $CaHPO_4$ does not exist as such in the insoluble phase. Undoubtedly, simultaneously with the chemical reaction, adsorption complexes are formed to a very considerable extent. There remains the other alternative that calcium aluminate might be formed under these conditions. This point has been studied by Line (11), who prepared these compounds by the precipitation method, mixing $Ca(OH)_2$ and calcium salts with the aluminates of sodium and potassium. When the precipitated calcium aluminate was added to a large volume of water it dissolved, and the solution deposited gelatinous aluminum hydroxide and was strongly alkaline. There is no possibility of calcium aluminate existing as a stable compound when the pH value of the solution is less than 8, as has been the case with our experiments.

It is noteworthy that when superphosphate solutions are added to a soil, the pH value may show a certain increase immediately after the addition of manure; but the soil solutions regain their old pH value in a very short time. It is clear from our experiments that this acid neutralizing power must be attributed not to the silicic acid constituents of the inorganic soil colloids but to the basic colloids like $Al(OH)_3$ and $Fe(OH)_3$.

It should also be noticed that the positive ions obtained from alumina gel by base exchange, as given in column 8 (table 9), is fairly large, unlike the case of pure silica gel (table 1). According to Michaelis, colloidal $Al(OH)_3$ is an ampholytoid, and Mattson (12) has found that below pH 7.4, colloidal alumina is electropositive. The origin of this positive charge may very well be, as Mukherjee (14) suggests, due to positive ions adsorbed on the surface by valency forces, and these are the ions which are replaced by calcium when the alumina gel is shaken with calcium dihydrogen phosphate solutions.

The curves shown in figure 1 bring out the effect on the adsorption capacity of adding silica to an alumina gel.

The adsorption capacity of silica gel is very small compared with that of the alumina gel; but it will be seen that as we add silica to a gel of pure alumina the adsorptive capacity of this mixture at first increases, reaches a maximum at the gel composition SiO_2 = 31 per cent, Al_2O_3 = 69 per cent, and then continually diminishes.

The adsorptive capacity of silica is very small compared with that of alumina. In table 10 are given the values of $1/n$ and K in the Freundlich equation,

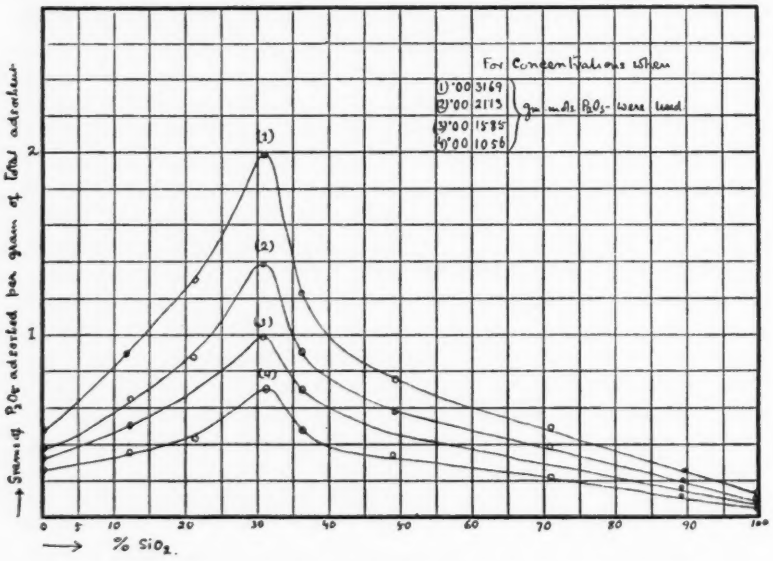

FIG. 1. EFFECT ON ADSORPTION CAPACITY, OF ADDING SILICA TO AN ALUMINA GEL

alumina being taken as the active adsorbing substance. These values have been obtained from the log x, log c, straight line as follows:

$$x = Kc^{1/n} \quad \ldots\ldots (A)$$

$$\log x = \log K + 1/n \log c \quad \ldots\ldots (B)$$

$$\frac{d \log x}{d \log c} = \frac{1}{n} \quad \ldots\ldots (C)$$

Thus $1/n$ is equal to the tangent of the angle of inclination of the log x, log c, straight lines to the log c axis. These values have been obtained from the graph, and by substituting these values in equation (B), the values of K have been calculated.

Obviously the greater the values of K and $1/n$, the greater is the absorptive capacity of the gel. It will be seen that the exponential factor, $1/n$, increases from 0.333 to 0.55 as silica is added to the alumina gel, but the value of this factor is almost independent of the composition of the gel. The value of K, which is also a measure of active surface, increases suddenly as silica is added to the alumina gel, passes through a maximum, and then diminishes as the percentage of silica in the mixed gel increases. Further investigation on this promoter action of silica is in progress.

TABLE 10

Values of 1/n and K when different amounts of silica are added to alumina gel

SAMPLE NUMBER	SiO_2	Al_2O_3	$1/n$	K
	per cent	*per cent*		
II	89.6	10.4	0.533	11.64
III	71.1	28.9	0.5416	17.06
IV	49.13	50.87	0.550	28.07
V	36.48	63.52	0.5052	79.80
VI	31.00	69.0	0.533	296.3
VII	21.7	78.3	0.542	36.65
VIII	12.3	87.7	0.550	10.12
IX	0.0	100.0	0.333	1.243

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